

CHEMICAL ABSTRACTS

Vol. 17.

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No. 1

1—APPARATUS

C. G. DÉRICK

Some features in condensing plant operation. G. F. HARDY. *Proc. Univ. Durham. Phil. Soc.* 6, II, 66-83(1921).—The lower tubes of a surface condenser transmit heat at a very low rate since in practice they largely cool air and do not condense steam. The displacement which an air pump would need to keep these lower tubes free from air would be excessive, since in that case the air would be removed at nearly steam temp. and therefore contain large vols. of water vapor. If some device could be applied to remove larger vols. of air from a condenser than is practical with an air pump, the duty of the condenser would be greatly increased. H. accomplished this by extg. the air with a steam jet, operated by steam from the engine driving the condenser auxiliaries. The wet air pump draws condensate through a by-pass around the jet; and draws air from the jet through a small contact condenser, which cools and devaporizes the discharge from the steam jet. Data are given on the performance of condensers before and after installing this device. They show a drop in temp. within the condenser of 31° F. without this device, of 1.5° to 5° with the device. W. L. BADGER

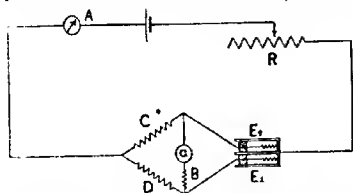
The nephelometer. I. N. KUGELMASS. *Compt. rend.* 175, 343-5(1922).—This app. was devised to study quant. the changes in the degree of aggregation of a colloidal system by the changes in the degree of transparence. It consists of an elec. lamp, a vessel for the colloidal soln., and a photo- or thermo-elec. cell fastened on a block, in a line, so that they can be placed in a const.-temp. bath. The lamp is placed in a small metallic chamber, blackened on the inside by camphor smoke. There is a groove in the chamber for inserting a filter for monochromatic light when colored solns. are being investigated. The side of the chamber facing the vessel is provided with a convex lens for producing parallel rays. The two faces of the vessel which are parallel are fitted, in their center, with circular apertures so that the light may pass through the soln. There is also in the vessel a hole fitted with a ground stopper for introducing the soln. The cell is of the same dimensions as the vessel, and the diameter of the sensitive part of it is the same as the diameter of the transparent portion of the vessel. It is connected to a millivoltmeter. The vessel is first filled with distd. H_2O and the no. of sec. necessary for the movement of the needle on the millivoltmeter 100 divisions noted. This is the unit of the "degree of transparence" (I). The distd. H_2O is then replaced by the colloidal soln. and the max. deviation of the needle (I') for the no. of sec. noted with H_2O , observed. Then I'/I gives the index of transparence. Expts. are recorded in which the app. was used to study the coagulation of fibrinogen.

G. W. STRATTON

A new practical colorimeter. ED. MOREAU and A. BONIS. *Ann. fals.* 15, 357-60 (1922).—Two glass cylinders having absolutely flat bottoms are graduated (to about 50 cc.) in mm., and supported on a suitable stand. One of the tubes (preferably the one contg. the standard soln.) has a side tube at the bottom, connected with a glass bulb and cock. Soln. is withdrawn from or added to the tube by blowing or sucking by means of a rubber bulb. Light is transmitted and colors are compared by means of a set of mirrors.

A. P.-C.

Electrical carbon dioxide recorders. G. A. SHAKESPEAR. *Electrician* 89, 543 (1922).—Most of the instruments now available for measuring CO_2 in flue gases depend on one or several chem. reactions; the chemicals have to be replenished from time



to time and besides there is the disadvantage of delicate glassware in the construction. The new recorder described is a decided improvement over these older types. The underlying principle of the new type: Two identical spirals of Pt wire are enclosed in two sep. cells, E_1 and E_2 (see fig.) in a metal block. Each of the spirals is connected to one arm of a Wheatstone bridge, the other 2 arms, C and D, being of manganin. Current flowing through the bridge heats the Pt spirals and causes them to lose heat to the walls of the cells. If the compn. of the gas of one cell is different from that of the other, the thermal cond. and hence the cooling rate will be different, giving rise to difference in temp. of the 2 wires. The difference in temp. will cause a deflection of the galvanometer, the greater the temp. difference the greater the deflection. One cell is filled with air and sealed and the other is exposed to the flue gas. A filter of glass wool and Fe borings is placed ahead of the open cell to protect the Pt. Further details are given.

C. G. F.

New rotary mercury pump. L. T. JONES. *Phys. Rev.* 18, 332(1921).—This pump is a liquid piston pump with Hg level remaining const. The rotation of an iron drum forces air from the high vacuum side along the axis of the drum to the low vacuum side where it is removed by an auxiliary pump capable of producing a vacuum of about 1 mm. The general performance is of the same order as that of the Gaede pump.

D. MACRAE

Simplest mercury vapor pump. L. T. JONES. *Phys. Rev.* 18, 332(1921).—A bulb contg. about 25 cc. of Hg is heated by a Bunsen burner and the vapor rises through a nozzle into a water jacketed chamber. The air intake is situated a little below the end of the nozzle but above the lower end of the water jacket. A fore pump capable of producing a vacuum of about 0.001 mm. removes the air from the top. Pyrex glass is used.

D. MACRAE

A new type of automatic temperature regulator and its application to heat-treating furnaces. R. W. NEWCOMB. *Trans. Am. Soc. Steel Treating* 3, 28-102(1922).—The regulator consists of 4 parts: the frame and bed plate, a $1/12$ h. p. motor with worm and worm gear speed reductions, an escapement or ratchet mechanism and a contractor. One sprocket, mounted on a ratchet wheel spindle, is connected by a sprocket chain to another sprocket wheel attached to the valve or other appliance to be regulated. When either one of the solenoids is energized one of the pawls of the escapement mechanism engages with the ratchet wheel and moves it in one direction or the other depending upon which pawl is engaged. The movement of the ratchet wheel depends upon the setting of the wrist pin at the cam. Proper selection of the sprockets can be made to correspond to open and closed valve positions.

W. A. MUDGE

The sieve centrifugal. BERTHOLD BLOCK. *Chem. App.* 9, 88-91, 117-20, 141-4, 153-6, 169-71, 177-9, 189-92(1922).—A discussion, with 58 cuts, of the construction of centrifugals with mech. discharge, semi-automatic centrifugals, continuously operating centrifugals, of the proper weave of the top sieve for materials of different grain, of the proper construction of the sieve backing to prevent clogging, of the proper clothing, with references to the literature and Ger. patents.

J. H. MOORE

Use of the respirator "Lix." K. MAIWALD. *Chem.-Ztg.* 46, 829-30(1922).—

This mask (Haase-Lampe, *C. A.* 15, 1363), designed to stop dust, may be used to stop vapors of alc., acetone, Et_2O , etc., by keeping the gauze filter moistened with H_2O .

J. H. MOORE

Vacuum adapter with cooling and heating device. C. A. ROJAHN. *Chem.-Zig.* 46, 830(1922).—A brief description, with 1 cut, of an app. which may be cooled or heated with H_2O , or heated with steam.

J. H. MOORE

An improved still for producing pure water. C. A. KRAUS and W. B. DEXTER. *J. Am. Chem. Soc.* 44, 2468-71(1922).—Pure H_2O with sp. cond. of 0.12×10^{-6} mhos is obtained by redistg. ordinary distd. H_2O in alk. permanganate soln. A still acting on the principle of fractional condensation is described. By its use H_2O with sp. cond. of 0.05×10^{-6} mhos may be obtained in quantity.

DONALD E. SHARP

Extracting sugar and other substances (Brit. pat. 184,453) 28.

Calorimeters. IGRANIC ELECTRIC CO., LTD. Brit. 183,400, April 7, 1921. In a continuous-flow gas calorimeter in which resistance thermometers are subjected to the initial and final temps. of a fluid which absorbs the heat of combustion, the thermometers are so constructed that their temp. resistance coeffs. vary in such a way that a const. relation between their resistances is maintained for a given calorific value of the gas, irrespective of the actual temp. level at which the test is carried out. The invention is described in connection with a calorimeter of the kind described in 153,817 (*C. A.* 15, 964), each of the thermometers contg., e. g., Ni and Cu in such proportions that the desired result is obtained despite variations in the sp. heat of the heat-absorbing air and in the vapor content of the test gas, caused by variations in the temp. of the water tank contg. the wet meters supplying the gas, etc. Cf. 18,495, 1914.

Calorimeters. IGRANIC ELECTRIC CO., LTD. Brit. 183,408, April 7, 1921. In a continuous-flow gas calorimeter, the burner and associated parts are so constructed that the stream of fluid which absorbs the heat of combustion is made to flow after such heat absorption in heat-exchanging relation with the same stream before or during the absorption of heat. Further, the products of combustion are made to flow in heat-exchanging relation with the combustible mixt. so as to preheat the latter.

Apparatus for the production of ozone. JNO. R. QUAIN. Can. 225,751, Nov. 7, 1922.

Specific gravity apparatus. E. G. BAILEY. Brit. 184,789, July 25, 1922. An instrument for indicating or recording the sp. gr. of a flowing liquid comprizes a vessel through which the liquid is passed and contg. a submerged float which is pivoted to the forked end of a lever, the other end of which carries a balance wt. The lever is secured to a spindle to which is also secured a pendulum so that as the float rises and falls the pendulum is moved until equil. is attained. To compensate for temp. variations, the float is made expansible by forming it with corrugations and it is filled with a liquid which may be the liquid to be tested at its normal sp. gr. The indication or record is obtained by a pointer, pen, etc., attached to the spindle.

Specific-gravity apparatus: K. WALBRER. Brit. 185,408, Aug. 28, 1922. An app. is specified for detg. the sp. gr. of solids by finding their wt. and vol.

Apparatus for mixing gases. F. MANGIAMELLI. Brit. 183,831, July 25, 1922. In app. for obtaining a mixt. of two gases issuing from their receptacles under different pressures, of the kind described in 151,785, for use with an oxy-acetylene welding pipe, the motor compressor, driven by one of the gases, is designed to compress an excess of the other gas, the excess being returned to the container.

Apparatus for adding reagents to liquids. I. G. FERRATT. Brit. 183,357, July 25, 1921. App. for adding powders to liquids, and particularly applicable for adding a

softening reagent to a domestic water supply, comprises means for intermittently delivering a given quantity of the liquid and a wheel arranged beneath a powder hopper and provided with measuring-pockets for the powder and rotated step by step by means actuated by the passage of the liquid to cause it to deliver the powder from one pocket on each delivery of liquid.

Apparatus for cooling, condensing, and heating. E. BARRS. Brit. 183,195, April 6, 1921. In app. for the cooling or heating of fluids, or the condensation therefrom of impurities, in which the cooling or heating medium is caused to pass between tubes, or the fluid to be cooled or purified is passed between rods, which tubes or rods extend through a series of compartments partitioned by plates having inlet and outlet openings, baffles are provided in planes at right-angles to the partition plates, sepg. the inlet and outlet openings and thus causing the fluid to travel around the compartments.

Filter. F. D'M. ACCIOLY. Brit. 183,784, April 20, 1921. A filter is fitted with 8 horizontal sieves covered with coarse woolen cloth and supporting, resp., in order from bottom to top, animal charcoal, fine sand, K_2CO_3 , animal charcoal, live lime, sand, animal charcoal, and $Ca(ClO_3)_2$, covered with filter paper paste. The material on the uppermost sieve is covered with woolen cloth on which is placed a perforated plate. The liquid is passed upwards through the filter.

Rabble apparatus for furnace. L. B. SKINNER. Can. 225,068, Oct. 24, 1922.

Mercury separator. JEROME HAVERLY. Can. 225,286, Oct. 31, 1922.

2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK

Samuel Wesley Stratton. ANON. *Elec. World* 80, 860(1922); 1 illus.—Biographical sketch. C. G. F.

Stimulating research by organization. T. S. TAYLOR. *Elec. World* 80, 961-2 (1922).—A clear and concise expression of an ideal research lab. organization. C. G. F.

Grasselli Medal award (to Walter H. Fulweiler). Presentation. HARLAN S. MINER. *J. Ind. Eng. Chem.* 14, 1154-5(1922). Acceptance. *Ibid* 1155. E. J. C.

Ernest Solvay—an appreciation. WM. H. NICHOLS. *J. Ind. Eng. Chem.* 14, 1156-8(1922).—An obituary. E. J. C.

Edgar Fahs Smith. W. T. TAGGART. *J. Ind. Eng. Chem.* 14, 1158(1922). E. J. C.

Manuscript bibliographies in chemistry and chemical technology. C. J. WEST AND CALLIE HULL. *J. Ind. Eng. Chem.* 14, 1075-8, 1148-51(1922). E. J. C.

The history of alchemy. E. O. VON LIPPIMANN. *Z. angew. Chem.* 35, 529-31 (1922). F. H.

Federal and state research agencies. W. M. CORSE. *Trans. Am. Soc. Steel Treating* 3, 231-8(1922).—An address. W. A. MUDGE

Research for engineering societies. A. D. FLINN. *Trans. Am. Soc. Steel Treating* 3, 218-25(1922).—An address. W. A. MUDGE

What progress has the new science of color brought? WILHELM OSTWALD. *Z. Elektrochem.* 28, 398-404(1922).—An address. H. JERMAIN CREIGHTON

Physico-chemical regularities in cosmic-chemical processes. SVANTE ARRHENIUS. *Z. Elektrochem.* 28, 404-11(1922).—An address. The question of the source of heat of cosmic bodies is discussed. H. JERMAIN CREIGHTON

Stellar chemistry. H. DINGLE. *J. Soc. Chem. Ind.* 41, 283-5R(1922).—General discussion. C. H. PARK

Atomic weights. R. J. MEYER. *Naturwissenschaften* 10, 911-8(1922).—A general

softening reagent to a domestic water supply, comprizes means for intermittently delivering a given quantity of the liquid and a wheel arranged beneath a powder hopper and provided with measuring-pockets for the powder and rotated step by step by means actuated by the passage of the liquid to cause it to deliver the powder from one pocket on each delivery of liquid.

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discussion including: (1) historical development; (2) the element of reference; (3) the international at. wt. commission; (4) the present status of research; (5) the German at. wt. commission and (6) the value of the most precise detns. C. C. DAVIS

The effect of variation in weight of the riders and plummets of the Westphal balance upon the accuracy of specific gravity determinations. F. A. TSCHUDY. *J. Am. Chem. Soc.* 44, 2130-35(1922).—Accurate d. detns. with the Westphal balance are possible only when the wt. of water displaced by the plummet at 15°, and the wts. of the riders possess an exact multiple relationship among themselves. Application of the corrections for any specific system of riders is facilitated by the construction and use of correction graphs. J. T. R. ANDREWS

Determination of the molecular weight of substances in alcoholic solution from the elevation of the flash point ROBERT WRIGHT. *J. Chem. Soc.* 121, 2247-50(1922).—The flash point of a combustible liquid may be regarded as the temp. at which the air space over the confined liquid is rich enough in vapor to permit the passage of flame through the air-vapor mixt. The method therefore depends on the vapor pressure lowering. The flash point can be detd. to within 0.1°. The flash-point const. or the elevation of flash point produced by the addn. of a mol. of solute to 100 g. alc. was calcd. to be 7.7. The mol. wt. of several solutes in alc. was detd. and the accuracy attained was comparable to that of the b. p. method. J. A. ALMQUIST

Preparation of pure ozone and determination of its molecular weight. SEBASTIAN KARRER AND O. R. WULF. *J. Am. Chem. Soc.* 44, 2301-7(1922).—Pure O₃ was prepd. as follows: Ordinary com. electrolytic O₂ purified and dried by passing through concd. H₂SO₄ and P₂O₅, was passed through an ozonizer and the resulting gases were condensed in a bath of liquid air. Fractional distn. of the blue liquid mixt. of O₃ and O₂ proceeded by allowing a slight rise in temp. At first O₂ with about 0.8% of O₃ came off, from which fact it is calcd. that the vapor pressure of O₃ at -182° is 6 mm. When a small portion of the liquid remains the temp. rises to -119°, the b. p. of O₃. This liquid was transferred to a mol. wt. bulb of known vol. and wt. At room temp. O₃ undergoes gradual decompn. to O₂ and a rise of pressure in the bulb is observed. The rate of pressure rise allows the calcn. of the pressure at the time when the O₃ reaches room temp. From 14 expts. the mean value of the mol. wt. is 47.3, corresponding to O₃. J. M. B.

Technical tensile strength and molecular strength. ADOLF SMEKAL. *Naturwissenschaften* 10, 799-804(1922).—A review of the recent work of Griffith (cf. *Trans. Roy. Soc. London* 221A, 163(1920)), Polanyi (cf. *C. A.* 16, 2053) and others, with a bibliography. C. C. DAVIS

Atomic domains in crystals. F. RINNE. *Umschau* 571-3(1922).—Numerical values of atonic and ionic diams. are derived by the crystal structure method of Bragg (*C. A.* 15, 2235) and essentially the same results obtained. G. L. CLARK

A photographic method of X-ray crystal analysis. ELMER DERSHEM. *Phys. Rev.* 18, 324(1921).—Abstract of X-ray photographic method particularly adapted for thin lamellar crystals. In the analysis by rotation many curved lines or streaks appear on the photographic plate, whose length and position depend entirely upon the slopes of the reflecting planes. With a single exposure it is possible to det. the distance between certain planes parallel to the axis of rotation by the spacing of characteristic lines, and the slopes of other planes by the above-mentioned streaks. G. L. CLARK

Optical demonstration of the Bragg method of crystal analysis. BILFRIED QUARDER. *Physik. Z.* 23, 350-2(1922).—Deductions by the Braggs of crystal structure from the intensity distributions in the spectra of different orders are justified theoretically and then exptly. by photographs of finely ruled lines on white cards. For the case where the lines of one lattice come midway between the lines of another interpenetrating lattice it is shown that the intensity of a given order I_p is proportional to $1/p^2 \left\{ \sin(a/g) \pi \right.$

$\mp \sin(b/g) \pi \nu \}^2$, where ν is the order, a and b are the different breadths of lattice lines corresponding to strongly and weakly reflecting atoms, and g is the lattice const.

G. L. CLARK

New revision of the density of oxygen. E. MOLES AND M. CRESPI. *Annales soc. espagn. fis. quim.* 20, 190-2(1922).—Oxygen prepd. from KMnO_4 always contains traces of CO_2 and O_3 and purification by P_2O_5 is insufficient. Detns. made on O_2 from KMnO_4 , purified by soda lime and metallic Hg, gave the value (calcd. for lat. 45°) 1.42895 for the wt. of the normal liter. This agrees well with values previously given.

L. E. GILSON

The solubility of phenanthrene in various organic solvents. HERBERT HENSTOCK. *J. Chem. Soc.* 121, 2124-9(1922).—The soly. app. employed was similar to that of Brönsted and Peterson (*C. A.* 16, 670). Purified materials were used. The data obtained agree with those of Hildebrand, Ellefson and Beebe (*C. A.* 11, 3146), except with CCl_4 . With a different soly. method for this solvent data were obtained which reduce the discrepancy. The soly. detns. are discussed from the standpoint of Pebble and Turner (*C. A.* 5, 2454) as to the relation between soly. and association in soln. Phenanthrene is not associated in MeOH , EtOH , petroleum or AcOH , but is associated in the other solvents, approaching the association of the solvent at higher temps. Soly. curves for CCl_4 , Et_2O and Me_2CO show marked breaks at 0, 10, and 15° , resp., ascribed to sudden alteration in association of phenanthrene at these points. HENRY C. PARKER

The solubility of helium in water. H. P. CADY, H. M. ELSEY AND EMILY V. BERGER. *J. Am. Chem. Soc.* 44, 1456-61(1922).—The soly. of He was detd. at 2° , 10° , 25° and 30° . The He, which was shown by spectroscopic examin. to be pure, was obtained from natural gas by liquefying most of the other components and absorption of the remainder in active coconut charcoal. The values of the coeffs. of soly. as calcd. from the equation $\alpha = 273.1 V_1/TV$ (where V is the vol. of H_2O , V_1 the vol. of He absorbed in V vols. of H_2O and T abs. temp.) are less than those obtained by other workers with the exception of one detn. by Ramsay. The soly. coeff. (0.00938 at 2° , 0.00838 at 30°) decreases with increasing temp., and there is no min. soly. In the app. used equil. was brought about by gentle stirring with a magnetic stirrer over a period of 24-36 hrs. Each detn. was made on a new sample of He and fresh water, so each is independent and a check of the others. The errors involved in the work of other investigators are pointed out.

G. W. STRATTON

Solubility and volatility of 3,5-dinitrophenol. N. V. SIDGWICK AND T. W. J. TAYLOR. *J. Chem. Soc.* 121, 1853-9(1922).—These properties for 5 of the 6 possible isomers of the above-named substance have already been measured. (Cf. *C. A.* 15, 3088.) 3,5-Dinitrophenol was prepd. by heating dry 3,5-dinitroanisole with two parts AlCl_3 at 120° until evolution of CH_3Cl ceased. The product was cooled, made strongly alk. and filtered. On acidifying the filtrate and cooling, the dinitrophenol crystd. out. The yield was 77 to 80% of theory. The product was purified by recrystn. from very dil. HCl , the dihydrate being obtained. The transition pt. to anhydrous salt is 53.9° , m. p. 126.1° . Soly. curves in H_2O and C_6H_6 and also volatility in steam were detd. The behavior of the 3,5 isomer is in accordance with the conclusions of the previous work.

A. E. STEARN

Solubilities of the alkali formates and acetates in water. N. V. SIDGWICK AND J. A. H. R. GENTLE. *J. Chem. Soc.* 121, 1837-43(1922).—Soly.-temp. data are given for the formates and acetates of Li, Na, K, Rb, and Cs. Evidence of hydrate formation was obtained in case of the formates of both Rb and Cs; no hydrate of K is noted. In general the soly. increases with the at. wt. of the metal, though Li and Na do not follow the rule in either of these cases.

A. E. STEARN

Solubilities of the alkali salts of benzoic and the hydroxybenzoic acids in water.

N. V. SIDGWICK AND ELINOR K. FyWBANK. *J. Chem. Soc.* 121, 1844-53(1922); cf. preceding abstr.—Soly. data for the Li, Na, K, Rb and Cs salts of BzOH and the 3 hydroxybenzoic acids are given. The hydroxybenzoates of Cs and Rb form hydrates in all cases; in the *m*-series neither the Li, Na nor K salt did. Thus the ordinary hydration rule does not hold here, and it is evident that in hydrate formation the cation is not the only detg. factor.

A. E. SYEARN

The solubility of the chlorophenols. N. V. SIDGWICK AND S. L. TURNER. *J. Chem. Soc.* 121, 2256-63(1922).—The soly. of the isomeric chlorophenols in water is characterized by abnormalities due to the position of the substituent. The crit. soln. temp. for the *o*- is much higher than that of the *m*- and *p*-comps. The abnormality is more marked at high temp. (soly. in water) than at low (soly. in benzene). This is an argument against the view that the abnormalities are due to the association of the *m*- and *p*-comps. since association diminishes with rise of temp.

J. A. ALMQUIST

The solubility of the aldehydobenzoic acids. N. V. SIDGWICK AND HERBERT CLAYTON. *J. Chem. Soc.* 121, 2263-7(1922).—The solubilities of the acids in water and benzene show that this group of isomerides is abnormal. As is the case with the hydroxybenzoic acids, the *o*-acid alone is capable of forming two liquid layers with water. The heats of soln. in benzene are calcd.

J. A. ALMQUIST

Solubility of oxygen in various organic solvents. Preliminary paper. FRANZ FISCHER AND GEORG PFLÜDERER. *Z. anorg. allgem. Chem.* 124, 61-9(1922).—O was pumped into a steel cylinder which contained the liquid, and the cylinder was shaken until equil. was indicated by a const. reading on a manometer. Part of the liquid was then withdrawn into a buret where the pressure fell to atm. pressure. The satn. pressure of the liquid was taken as the mean of the cylinder pressures before and after sampling. The following results were obtained for the cc. of O (standard conditions) dissolved in 1 cc. of the liquid. Water at 20°, 0.021; 0.1 *N* aq. KOH at 20°, 0.024; petroleum ether (b. p. below 65°) at 18.5°, 0.409; benzene (h. p. 65-100°) at 18°, 0.292; com. petroleum at 18°, 0.159; paraffin oil at 18°, 0.114; CHCl₃ at 18°, 0.205; CCl₄ at 18°, 0.230; C₂H₅Cl at 18°, 0.100; MeOH at 19°, 0.175; EtOH (96%) at 20°, 0.143; isoamyl alc. at 17°, 0.163; acetone at 19°, 0.207; Et₂O at 20°, 0.415; EtOAc at 20°, 0.163; C₆H₆ at 19°, 0.163; C₂H₄ at 18°, 0.168; xylene at 16°, 0.169; nitrobenzene at 18°, 0.070; tetracyclonaphthalene at 17°, 0.094; pyridine at 18°, 0.099.

J. M. B.

Selective solvent action by the constituents of aqueous alcohol. ROBERT WRIGHT. *J. Chem. Soc.* 121, 2251-6(1922).—The effect of 3 solutes, sucrose, benzyl alc. and glycerol, on the partial vapor pressures of 38% aq. alc. was investigated. Sucrose (sol. in water, insol. in alc.) lowered the vapor pressure of water and raised that of alc.; benzyl alc. (sol. in alc., insol. in water) lowered the vapor pressure of both components; glycerol (sol. in both) lowered the vapor pressure of water and raised that of alc. The results in each case depend on the solute used and could not be predicted from the action of the solute on the sep. pure components of the solvent.

J. A. ALMQUIST

Index of refraction of water, ethyl alcohol, and carbon disulfide at various temperatures. A. R. PAYNE AND E. E. HALL. *Phys. Rev.* 18, 326-7(1922).—This brief abstract of a paper read before the Am. Phys. Soc. states that the *n* of H₂O was measured by the spectrometer method from 16° to 98.4°, Et₂O from 15° to 75°, and that of CS₂ from 16° to 45°. No data are given.

D. MACRAE

The physical constants of ozone. E. H. RIESENFELD AND G. M. SCHWAB. *Z. Physik* 11, 12(1922); cf. C. A. 16, 3416.—Density of O₃ was detd. between -112 and -183°; it is well represented by the formula $1/d = a + bT + cT^2$, in which $a = 0.51193$, $b = 0.04559$, and $c = 0.03929$ and T is abs. temp. By the rule of rectilinear diameter d is 0.537. The critical pressure, b. p., and mol. vol. at h. p. are calcd. by the classical theory of corresponding states and by Byk's "quantum theory of corre-

sponding states" (*C. A.* 16, 1695). Values by the latter agree better with exptl. results. The fact that values calcd. on basis of classical theory do not differ markedly from expt. is held as proof that O_3 is free of O_2 (which deviates from classical theory) and also of any polymers.

BENJAMIN S. NEUHAUSEN

The field of colloid chemistry. The study of structure. R. ZSIGMONDY. *Z. angew. Chem.* 35, 449-51(1922).—The study of colloids is divided into at least 3 fields, colloid physics, colloid chemistry, and a study of structure. There are 3 kinds of colloidal particles: a primary or A particle also called a *protone*, a secondary or B particle called a *polyone*, and a *vacillone*. The protone is a particle from 2 mm. to 40 mm. in diam. and composed principally of the dispersed substance. A polyone is a suspended particle composed of many protones which cling together but also enclose much of the suspending medium. When 2 liquids are completely miscible at one temp. and not at others, near the critical region, particles form which are neither protone or polyone. They are vacillones.

F. E. BROWN

The theory of mechanical colloid synthesis. F. SEKERA. *Kolloid-Z.* 31, 137-49 (1922).—Each method of colloidal dispersion presents 2 problems: the reduction of the material to particles of colloidal dimensions, and the preservation of the small particles by charging them electrically. Particles of colloidal size can be prepd. by an impact at a speed of 40 m./sec. or faster; or with less energy by the principle of the "Wasserschusses"; or in the case of elastic material as rubber by phys. action and the addn. of a little org. solvent; or by pouring a soln. of material insol. in water into water and distg. off the org. solvent. Particles of solid formed by any one of these methods have latent valencies and tend to reunite. These latent valencies are the same forces which hold atoms in the space lattice of crystals. There will be both positive and negative valencies exposed on the particles. Which of the valencies is effective in absorbing ions depends on the ions present. The ion which attaches to the colloidal particle will be the ion which would form an unionized or insol. mol. with the single radical of opposite charge to which it unites. That is, a colloidal particle composed of AgI takes up Ag^+ from an excess of $AgNO_3$ and I^- from an excess of KI. After the union with ions the particles will all bear the same charge and have less tendency to unite with each other. The central portion of the colloidal particle is designated by the term "Ballast," the adsorbed ions by the term "Trager." The stability of the colloid is a function of the size of the "Ballast" particles and of the dissociation of the supporting electrolyte. For com. purposes colloids must be transported in a coned. form. It is possible to prep. a sol directly from the colloid machine. Besides the electrolyte a protective colloid must be added while conen. is being carried out. This keeps the electrolyte from forming in crystals. The residual valencies of the "Ballast" particles are kept apart and the colloid is reversible.

F. E. BROWN

The "cloud process," a new method for the preparation of colloids. F. SEKERA. *Kolloid-Z.* 31, 148-9(1922).—Colloidal particles can be prepd. by dissolving the chosen material in some suitable solvent and then spraying the soln. into a room warm enough to evap. the solvent. The solute will be left suspended in very small particles. The size of the particles depends on the conen. of the soln., the degree of dispersion of the spray, and the temp. at which evapn. takes place. At temps. above the h. p. of the solvent the particles of solute may burst into yet smaller particles. Substances whose b. ps. are higher than that of the solvent may be added to the soln. After evapn. they will be on the colloidal particles. In this way ionogens of high mol. wt. can be introduced as stabilizing agents. The method has been tried for S dissolved in CS_2 . F. E. B.

Sulfide sols. III. The preparation of sols by hydrolysis. F. V. V. HAHN. *Kolloid-Z.* 31, 200-3(1922); cf. *C. A.* 15, 3777.—By hydrolysis of alkali stibiothiosulfate (Szilagy, *C. A.* 15, 2597) various sulfide sols can be prepd. By means of a modified

form of the *Mann dialyzer* (*C. A.* 15, 1326), which is particularly advantageous for estg. the salts contained in the dialyzate, the equations for the hydrolysis of stibiothiosulfates given by v. S. were confirmed. Ultramicroscopic examn. of the dialyzed colloid and ultrafiltration show that it decomposes very rapidly, especially at higher concns. A sol of over 0.4 molar concn. does not exist, probably because the electrolyte formed with it causes it to flocculate and to sep. out. The sol of $\text{Li}_3\text{Sb}(\text{S}_2\text{O}_3)_3$ is the most stable, the K salt is next and the Na salt is the least stable. A. MUTSCHELLER

Colloidal calcium hydroxides. M. v. GLASENAPP. *Kolloid Z.* 31, 195-6(1922).—While examg. the hardening process of Roman cement (compn. given), G. observed two forms of colloidal $\text{Ca}(\text{OH})_2$; these are described and illustrated with photographs. There was first formed a primary colloid in small drops, which grew slowly. In this primary colloid, probably with H_2O elimination, the secondary colloid was formed; it grows until, with adjoining drops, it forms cryst. $\text{Ca}(\text{OH})_2$. A. MUTSCHELLER

The colloids arabic acid and arabic acid plus gelatin. F. W. TIEBACKX. *Pharm. Weekblad* 59, 1014-29, 1056-63(1922); cf. *C. A.* 16, 2433.—Cond. measurements, osmotic-pressure, freezing point and viscosity detns., and ultramicroscopic examn. show that arabic acid is an electrolyte. The flocculation of a mixt. of arabic acid and gelatin by dil. HCl is due to salt formation in which equil. occurs at H-ion concn. of 10^{-4} . A. W. DOX

An investigation of the electrical properties of silicic acid sols. OTTO LÖSENBECK. *Kolloidchem. Beihefte* 16, 27-46(1922).—The addn. of silicic acid sol decreased the cond. of solns. of HCl , at first rapidly and then always less, according to an e -function. The curve finally approached asymptotically the limiting value. The migration velocity of SiO_2 particles was detd. experimentally and substituted in Smoluchowski's equation in order to calc. the contact potential. This equation (cf. *Krak. Anz* 1903, 182) is $U = V/k/4\pi\eta$, in which U is the migration velocity for a field strength of 1 E. S. unit, V is the p. d. of the double layer in E. S. units, k is the dielec. const. for H_2O and η is the viscosity of H_2O in C. G. S. units. As shown by cataphoresis, the SiO_2 particles were negatively charged. This negative charge decreased with each addn. of HCl to zero at the isoelec. point and finally the particles assumed a positive charge greater than the negative charge for the acid-free sol. The behavior of the SiO_2 particles was not uniform. Measurements for different concns. of the same sol showed the contact potential to be dependent on the concn. To explain the observed facts the suggestion is made that the SiO_2 particles absorb the HCl like a sponge. H. M. McLAUGHLIN

The effect of anions, especially of the hydroxyl ion, on the colloidal state of night blue. S. AKAMATSU. *Kolloid Z.* 31, 209-15(1922).—Ordinarily, the OH^- ions are the most active in their effects upon colloids and should, therefore, be at the head of the anions of the Hofmeister series. Expts. of I. Traube (*C. A.* 7, 438), however, place OH^- after Cl^- , which is in contradiction with the usual conception. Night blue is a basic positive colloidal dye. Changes in the surface tension were detd. by a Traube stalagmometer. The results are given in tables and curves and in general confirm the results of Traube. To measure the OH^- concn. A. dialyzed 10 cc. of the dye sol to which increasing additions of KOH had been made, against 10 cc. of pure water and detd. the OH^- in the dialyzate by the indicator method. OH^- is considerably more active than the Br^- , I^- or CNS^- . The position of OH^- in the Hofmeister series assigned by Traube is, therefore, incorrect, but it possesses the same exceptionally high effectiveness which it is known to possess toward the electropositive ions. A. MUTSCHELLER

Influence of the temperature on the coagulation of colloidal gold. H. LACHS AND S. GOLDBERG. *Kolloid-Z.* 31, 116-9(1922).—The influence of temp. on the coagulation of colloidal Au was investigated with samples prepd. by 4 different methods. The time of coagulation was found to be inversely proportional to the abs. temp., a

result which follows from Smoluchowski's theory (*C. A.* 11, 3140). The coagulation velocity of colloidal Au is much less sensitive to change in temp. than is usual for chem. reactions.

HARRY B. WEISER

Colloid solutions of carbon in water. P. C. L. THOMR. *Kolloid-Z.* 31, 119-32 (1922).—A survey of the literature on colloidal C is followed by an exptl. investigation on the prepn. and properties of colloidal sols of amorphous C and graphite. Sols of C may be prepd. (1) by anodic disintegration, (2) by chem. oxidation, (3) by decompn. of org. compds. Sols prepd. by the first method had a high C content but were never pure. Complex C compds. were doubtless formed and were adsorbed by the colloidal particles, giving the colloid its stability. Expts. were carried out on colloidal graphite prepd. by anodic disintegration and on Acheson's "aquadag." The action of electrolytes on the latter showed that it was a negative colloid. Cations arranged in the order of decreasing pptg. power are: $Al > Ba > H > Na > NH_4$. Technical applications of colloidal C are mentioned.

HARRY B. WEISER

Ultrafiltration of soap solutions. Sodium oleate and potassium laurate. J. W. MCBAIN AND W. J. JENKINS. *J. Chem. Soc.* 121, 2325-44 (1922).—A theory of ultrafiltration through permeable and semipermeable membranes is developed on the basis that only those constituents the diams. of which are less than that of the pores will pass through any given pore and that nothing will pass through any given pore unless the pressure in use exceeds the osmotic pressure of every other constituent that is coarse enough to be held back. The whole range of possible pressures is, therefore, divided up by certain critical osmotic pressures, at which sharp breaks occur in the compn. of the filtrate. Ultrafiltration methods have confirmed the values, deduced by other methods, for hydrolysis, osmotic pressure, and amts. of crystalloidal and colloidal matter of K laurate and Na oleate. The values obtained are given in several tables. The hydration of soap is defined as the total number of g. mols. of H_2O chemically combined with or adsorbed by 1 g. equiv. of soap. This hydration can be measured by means of ultrafiltration and use of a suitable neutral reference substance. The extent of the increase on concn. of the reference substance found in the filtrate above that in original soln. is a measure of the H_2O abstracted by the colloid from the soln. Soap in soln. contains at least 10 mols. of hydrate H_2O per equiv. of soap. The soap when in a true soln. behaves as a crystalloid, but the undissociated soap may be aggregated to form particles of neutral colloid, whereas if the fatty ions are aggregated without loss of elec. charge, they form colloidal particles known as ionic micelle. This ionic micelle has been sepd. from neutral colloid by ultrafiltration. The diam. of the particles of ionic micelle is only a few times the length of a mol., and its approx. formula is $(OI^-)_{18}mH_2O$. The particles of neutral colloid of K laurate are less than 15μ in diam., those of Na oleate about 10 times larger.

E. F. PERKINS

Metachromatism of toluidine blue. ROBERT SCHWARZ AND ERIKA HERRMANN. *Kolloid-Z.* 31, 91-4 (1922).—By the use of silicic acid gel, $BaSO_4$, $Al(OH)_3$, and $MgNH_4PO_4$ as absorbing agents for the dye, it was shown that the cause of metachromatism may be attributed to the degree of dispersion of the medium taking up the dye and to the nature of the charge on the surface as detd. by the adsorption of ions. H. M. McL.

Adsorption. MAX GELOSO. *Ann. chim. anal. chim. appl.* 4, 293-8 (1922).—A general discussion of the theories of Perrin, Reichler, Gibbs, and Freundlich applied to adsorption by ppts. From his own work (*C. A.* 16, 3018) G. believes adsorption may be due to mutual pytn. of colloids.

BENJAMIN S. NEUBAUSSEN

Absorption of air by charcoals at low temperatures. K. HAYASHI. *J. Chem. Soc. Japan* 43, 535-44 (1922).—In order to discover a charcoal which would absorb air more than coconut charcoal, H. detd. cc. of air adsorbed by com. charcoals and by those prepd. in the lab. The results are as follow:

	Bulk density.	Pres. source.	Cc. absorbed (at 0° and 760 mm.) by 1 g. —185° C. —79° C. 0° C. Room temp.				
(A) Com. charcoal							
Kuri-sumi (Chestnut).....	0.33	761	139.24	46.23	10.17	7.15	(13°)
Moku-Tan.....	0.40	767	119.71	43.19	15.34	12.65	(14°)
Nara-Sumi (evergreen oak)...	0.46	764	96.64	30.67	6.65	5.00	(11°)
Mixed charcoal.....	0.92	754	76.67	34.46	7.54	6.32	(11°)
Keyaki-sumi.....	0.66	747	48.06	10.88	2.08	0.68	(12°)
Kata-sumi.....	0.65	766	...	34.77	10.31	7.93	(13°)
(B) Prepd. in lab.							
Cherry charcoal.....	0.21	757	134.65	41.44	12.84	11.52	(16°)
Hashi-sumi (<i>Quercus dentata</i>)	0.30	757	132.45	...	10.05	7.47	(16°)
Kashiwa-sumi.....	0.39	758	44.18	24.53	7.95	7.34	(16°)
Cedar charcoal.....	0.19	762	112.12	...	3.48	2.14	(15°)
Pine charcoal.....	0.12	762	120.24	...	7.24	4.66	(17°)
Bamboo charcoal.....	0.48	770.7	121.53	47.68	15.96	12.28	(13°)
A-tan charcoal.....	0.57	759	66.07	...	5.10	2.83	(14°)
Coconut charcoal.....	0.98	760	120.79	38.19	10.62	8.88	(12°)
Pine-cone charcoal.....	..	766	103.92	24.67	8.91	5.31	(15°)
Walnut charcoal.....	..	764	101.42	...	3.23	2.35	(14°)
Chestnut charcoal.....	..	759	72.22	28.18	9.72	8.07	(12.5°)
Blood charcoal.....	..	764	45.73	...	13.66	8.49	(12°)
Bone charcoal.....	..	761	36.84	6.61	2.25	1.99	(15°)
Sugar charcoal.....	..	761	27.95	15.15	4.95	4.33	(14°)
Acorn charcoal.....	..	763	16.60	...	3.23	2.75	(13°)
Caster-bean charcoal.....	..	766	...	13.90	6.02	4.09	(17°)
Silica gel.....	..	765	63.08

Bulk d. of the last 9 charcoals (because they were powders) could not be detd. Gram for gram, coconut charcoal does not absorb more air than the others, but on account of high bulk d., its absorption is far greater if compared on the basis of vol. The app. and the method of detn. of bulk d. are described in detail. S. T.

A kinetic theory of adsorption. D. C. HENRY. *Phil. Mag.* 44, 689-705(1922).—A theory of the adsorption of gases is developed on a kinetic basis, assuming Langmuir's conception of a monomol. layer. Equations for the adsorption isotherm and isostere are deduced and shown to be in satisfactory agreement with expts. for N_2 , CH_4 , CO , and CO_2 . The consts. involved in adsorption by charcoal are given for a no. of gases. Adsorption from soln. is also treated and the well known formula, $x = kc^{1/n}$, is deduced from surface energy and osmotic considerations, and theoretical significance is proposed for the exponent through the relation: $1/n = (\text{osmotic work in adsorbing } x' \text{ g. mols.}) / (\text{total work in adsorbing } x' \text{ g. mols.}) = RT / (RT + W)$, where W is the non-osmotic work in adsorbing 1 g. mol., which is probably the work done in the surface orientation of the mols. and should not vary much with temp. Therefore $1/n$ is a quantity always < 1 , which tends toward 1 with rise of temp. The theory advanced is not claimed to be a complete soln. of the problem, but the agreement obtained is sufficient to indicate that the mechanism of adsorption suggested may not be far from the truth. S. C. LIND

Equilibrium in aqueous solutions of the alkali metal bisulfites. E. C. C. BALY AND R. A. BAILEY. *J. Chem. Soc.* 121, 1813-21(1922).—The solns. were investigated by a study of the absorption spectra. In aq. solns. of bisulfite there is a small amt. of metabisulfite absorbing light of wave length 257μ . These solns. are stable in light in the absence of O_2 ; otherwise a photo-oxidation of the HSO_3 ion takes place, producing normal sulfate, sulfurous acid and hydrated SO_2 . The soln. then shows the absorption band at $\lambda = 276 \mu$ characteristic of the last-named substance. The following equilibria

exist in air-free solns. of bisulfite or metabisulfite: $2\text{KHSO}_3 \rightleftharpoons \text{K}_2\text{S}_2\text{O}_5 \rightleftharpoons 2\text{K}^+ + \text{S}_2\text{O}_5^{--}$ and $\text{KHSO}_3 \rightleftharpoons \text{K}^+ + \text{HSO}_3^-$. On exposure to air and light the following changes occur: $\text{K}^+ + \text{HSO}_3^- + \text{O} \rightarrow \text{K}^+ + \text{HSO}_4^-$; $\text{HSO}_4^- \rightarrow \text{H}^+ + \text{SO}_4^{--}$; $\text{K}^+ + \text{H}^+ + \text{SO}_4^{--} \rightarrow \text{K}^+ + \text{HSO}_4^-$; $\text{K}^+ + \text{HSO}_3^- \rightarrow \text{K}^+ + \text{K}^+ + \text{SO}_4^{--} + \text{H}^+ + \text{HSO}_3^-$; $\text{H}^+ + \text{HSO}_3^- \rightleftharpoons \text{H}_2\text{SO}_3 \rightleftharpoons \text{SO}_2 \cdot x\text{H}_2\text{O}$. No isomerism of sulfite mols. was detected. The absorption bands of sulfurous acid, bisulfite and sulfite lie in the extreme ultra-violet. The characteristic ultra-violet frequencies of SO_2 , $\text{SO}_2 \cdot x\text{H}_2\text{O}$ and $\text{K}_2\text{S}_2\text{O}_5$ are integral multiples of the fundamental mol. frequency of SO_2 in the infra-red. A. E. STRAIN

The free energy of dilution of alcoholic solutions of lithium chloride and the effect of solvent upon the activity of ions. J. N. PHARCE AND H. B. HART. *J. Am. Chem. Soc.* **44**, 2411-19(1922).—From the measured e. m. f. at 25°, 30°, and 35°, of concn. cells, with and without ion transference, contg. alc. solns. of LiCl, the transference nos. of the Li ion were found to be approx. the same as in water. Decrease in free energy and heat content accompanying changes in concn. were calcd. The e. m. fs. of cells contg. alc. soln. of LiCl of concn. (C) against 0.1 M aq. solns. of LiCl were measured at the above temps. and the free energy and heat content changes calcd. F. N. BUNTING

Conductance of solutions of salts in phenol at 50°. C. A. KRAUS AND H. F. KURTZ. *J. Am. Chem. Soc.* **44**, 2463-8(1922).—The cond. of solns. of Me_4NI and of NaI in phenol were measured. C. R. PARK

Conductance of aqueous solutions of iodic acid and the limiting value of the equivalent conductance of the hydrogen ion. C. A. KRAUS AND H. C. PARKER. *J. Am. Chem. Soc.* **44**, 2429-49(1922).—Measurements were made in glass and quartz cells with water of varying degrees of purity. The cond. curves exhibit a max. due to impurities and soln. of the alkali from the glass. Measurements in quartz cells were made with concns. as low as $5 \times 10^{-4} N$. The value of λ_0 at 25° is 389.55. The value of $\lambda_{\text{IO}_3^-}$ is 39.62 and that of λ_{H^+} is 349.93. C. R. PARK

Effects of surface tension. P. B. GANGULY AND B. C. BANERJEE. *Z. anorg. allgem. Chem.* **124**, 140-2(1922).—A stick of NaOH immersed perpendicularly in distd. H_2O shows max. attack where the surface of the solvent comes in contact with the solid. Similar results were obtained with sticks of KOH, NaNO_3 , CuSO_4 , and ZnCl_2 . The more sol. the substance, the greater the effect. Large crystals of easily sol. compds. act in like manner. Rods or wires of Zn, Cu, Al, brass, Cd, Ni, and Mg perpendicular in dil. H_2SO_4 are dissolved most at the surface of the acid. G. and B. believe that surface tension acts to supply fresh solvent as the heavy satd. layers of soln. sink. An Fe rod half immersed in HCl in a long tube is etched to a point at the lower end; this is because Fe is more sol. in the presence of Fe^+ salts which sink toward the lower end of the rod. A Cu rod acted similarly in NH_4Cl - NaNO_3 soln. The effect is reversed when Fe or Zn is immersed in CuSO_4 ; a raised ring is formed at the surface boundary, surface tension supplying fresh Cu^+ ions. The addition of a substance like C_6H_6 or oil to lower the surface tension greatly diminishes these phenomena. M. O. LAMAR

Reaction of methane and also of acetylene upon zirconium tetrachloride. F. P. VENABLE AND R. O. DEITZ. *J. Elisha Mitchell Sci. Soc.* **38**, Nos. 1 and 2, 74-5 (1922).— ZrCl_4 reacts with NH_3 , PH_3 and H_2S forming compds. which, when heated, yield Zr nitride, phosphide, and sulfide, resp. Zirconia reacts with C at high temp. forming ZrC . ZrCl_4 was volatilized while CH_4 was passed through the reaction tube. The ZrCl_4 darkened at 400°. Three distinct products remained after washing: black particles, light brown particles, and colorless masses with black inclusions. The black particles analyzed 32.09% C and were only a small % of the original mass. The reaction with C_2H_2 began on gentle heating and was exothermic. HENRY W. EASTERWOOD

The reciprocal action of two metals dissolved in mercury. G. TAMMANN AND W. JANDER. *Z. anorg. allgem. Chem.* **124**, 105-22(1922).—Usually the detn. of the affinity of both components in crystals of a singular compn. is carried out at elevated temp.

Affinity values so obtained may be controlled (a) by a detn. of the lowering of the f. p. and comparison of the value found with that of the 2 components, (b) by measuring the effect of a metal in definite concn. on the tension-concn. curve of the other metal dissolved in a third noble liquid metal. These methods are applied to several pairs of metals, the compn. diagrams of which are known, with Hg as solvent. If the tension of the amalgam after the addition of the noble metal *B* is detd. by the concn. of the base metal *A*, equal tensions of the binary and ternary amalgams correspond to equal concns. of the base metal. If the tension curve of the binary amalgam is known, for every tension of the ternary amalgam the corresponding concn. of the uncombined noble metal can be deduced. If *x* represents that concn. there follows from the mass law $\{(A-x) + (A-x)(n_{AB}/m_{AA})\} + x^m [B-(A-x)(n_{AB}/m_{AA})] = k$, where *A* and *B* represent the total concn. of the 2 metals dissolved in Hg and *a_A* and *a_B* their at. wts. For ternary alloys with const. concn. of noble metal the 2 cases are distinguished: (1) where the compd. of the 2 metals dissolved in Hg is completely dissociated, (2) where it is entirely undissociated. Amalgams of the noble metals were prepd. by weighing, those of base metals by quant. electrolysis. Tension curves were studied of the following series: Zn, Zn-Cu, Zn-Ag and Zn-Au amalgams; Cd, Cd-Cu, Cd-Ag and Cd-Au amalgams; Pb, Pb-Ag and Pb-Au amalgams; Co-Sn, Co-Bi and Mg-Sn amalgams. Many curves and tables.

M. O. LAMAR

Reversibility of the reaction between nitrogen, carbon and sodium carbonate. C. K. INGOLD AND DANIEL WILSON. *J. Chem. Soc.* **121**, 2278-86(1922).—N was passed over a boat contg. Na₂CO₃ and C in known amts. and CO was passed over a known amt. of NaCN; in each case Fe was used as a catalyst. The total pressure of the gases and the temp. of boat were known and could be kept const. The compn. of the equilibrated liquid phase was detd. by rapidly cooling and analyzing the product in the boat. True equil. was taken as the mean of the values obtained by approaching from the Na₂CO₃ and C side and from the NaCN and CO side. Consistent results were obtained at temps. near 900°. Below this temp. it is difficult to bring the expt. to completion and much above 900° the volatility of NaCN causes appreciable losses from the boat if the reaction were allowed time for completion. The reaction is $N_2 + 4C + Na_2CO_3 = 3CO + 2NaCN$. The law of mass action applied to the gaseous phase for a const. temp. gives the following relation, which is carefully worked out and found to be theoretically correct and also to agree within 1% with the exptl. data obtained over a wide range of variable conditions: $\log_{10} \left\{ \frac{[X^2/(1-X)] [(1-P)^3/P]^2}{\alpha + (\beta/T)} \right\} = \alpha + (\beta/T)$, where *X* is the proportion of combined Na which is in liquid phases as NaCN (that is, the yield of NaCN), *P* is partial pressure of N calcd. as fraction of total pressure of N and CO, α and β are constns. which are found exptly. to be 23.91 and -31,180, resp., and π stands for the total pressure of N and CO.

E. F. PERKINS

Oxidation of nitrogen tetroxide by ozone. O. R. WULF, FARRINGTON DANIELS AND SEBASTIAN KARRER. *J. Am. Chem. Soc.* **44**, 2398-2401(1922).—The reaction between N₂O₄ and O₃ at 25° is instantaneous. Quant. titrations, with the disappearance of brown fumes as the end point, show that one mol. of O₃ is required for each mol. of N₂O₄. One atom of the 3 in ozone is available for the oxidation, in contrast to the oxidation of SO₂ to SO₃ by O₃ at temps. below 40°, in which all 3 of the O atoms are available for oxidation.

JAMES M. BELL

Decomposition of nitrogen pentoxide in the presence of ozone. FARRINGTON DANIELS, O. R. WULF AND SEBASTIAN KARRER. *J. Am. Chem. Soc.* **44**, 2402-4(1922).—Pure N₂O₅ in the presence of O₃ appears to have a much slower rate of thermal decompn. than N₂O₅ which is partially decomposed. The decompn. is thus apparently autocatalytic. Small traces of the decompn. products are sufficient to obtain a const. sp. rate of decompn.

JAMES M. BELL

Free and total energy changes in the reduction of quinones. J. B. CONANT AND L. F. FIESER. *J. Am. Chem. Soc.* **44**, 2480-93(1922).—Temp. coeffs. of the oxidation-reduction e. m. f. of derivs. of benzoquinone, naphthoquinone and anthraquinone were measured and the free energy, total energy and latent heat of reduction in aq. soln. calcd. Similar measurements in alc. soln. were also made. An equation giving the free energy change in terms of the potential and the solubilities of the quinone and hydroquinone was developed. E. N. BUNTING

Equilibrium of sodium and potassium salts at low temperatures. MARIO AMADORI. *Atti ist. Veneto* **79**, 293(1919).—The miscibility of the three pairs of Na and K salts (chloride, nitrate and sulfate) in the solid state is practically nil. Their behavior when in equil. with their satd. solns. is characteristic. The chlorides and nitrates sep. pure from a soln. of Na and K chloride and nitrate. However, for the chlorides there is a decrease in the soly. of each salt, while in the case of the nitrates there is an increase. The sulfates also sep. as pure salt from the mixed soln. The compound $3K_2SO_4 \cdot Na_2SO_4$ can be isolated, providing Na_2SO_4 is present in excess of the theoretical amt. necessary for the formation of the compd. The indication is that this is a definite compd., and is not miscible with its components. Numerous tables of solubilities, as well as cryoscopic data on mixts. of these salts are included. A. W. CONTIERI

Velocity of reaction in mixed solvents. III. Influence of temperature on velocity of saponification of esters. HAMILTON MCCOMBIE, H. A. SCARBOROUGH AND R. H. SETTLE. *J. Chem. Soc.* **121**, 2308-18(1922).—The velocity of reaction between Et esters of certain acids and KOH in EtOH-H₂O mixts. over a range of 15-45° was examd. in order to obtain information as to the persistence of complexes between EtOH and H₂O at definite temps. The curve showing the relation between the velocity-of-reaction const., *K*, and % compn. of solvent is divisible into a series of straight lines. The points of intersection of these straight lines occur at such compn. of solvent as correspond with simple EtOH-H₂O complexes. Six such complexes seem to be indicated, the compn. being: 5EtOH.3H₂O, 2EtOH.3H₂O, EtOH.3H₂O, EtOH.4H₂O, 3EtOH.5H₂O, and EtOH.6H₂O. The complex formed does not depend on the nature of the ester except in case of the *o*-substituted aromatic esters, where a complex 2EtOH.3H₂O appears to be formed in preference to the complex 3EtOH.5H₂O. The stability of a complex appears to be dependent on the temp. since the complex EtOH.4H₂O is not observed at 30° and complexes 3EtOH.5H₂O and 2EtOH.3H₂O are not apparent at 45°. The temp. coeff. is dependent on compn. of solvent, falling steadily as % of H₂O is increased until a minimum value of 2 per 10° is reached. E. F. PERKINS

The velocity of reaction of oxygen, hydrogen sulfide, and halogens with metals. G. TAMMANN AND W. KOSTER. *Z. anorg. allgem. Chem.* **123**, 195-224(1922).—Thin sheets of several metals of equal area were subjected to the action of halogens, O₂, air and H₂S in small elec. heated glass tubes at temps. of 15-644° for 1 to 20 min. The tempering colors formed were noted and compared with the thickness of the compd. formed by reaction. In many instances the tempering colors give comprehensive data of the speed of the reaction. In general the speed of the reaction varied directly with the temp., mass of metal, and concn. of gases. Calcns. of the thickness of the reaction product in μ from derived formulas agreed very closely with observed results. In Cl the velocity was Cu > Pb > Ag; in Br, Ag > Pb > Cu; in I, Pb > Cu > Ag; in N-O mixts., Fe > Cu > Ni, with decreased reaction for decreasing percentages of O; in air, Cd > Sn > Pb > Mn > Zn > Co; and in H₂S, Cu > Mn > Ag > Pb. W. A. MUDGE

Velocity of formation of some nitrides. G. TAMMANN. *Z. anorg. allgem. Chem.* **124**, 25-35(1922).—The rate of action of a gas on a metal can be detd. by observation of the color changes of the metal, which are due to changing thicknesses of the layer of reaction

product. Where the action of the gas on the metal is rapid, such observations det. the rate of diffusion of the gas through the surface layer. Metal surfaces were exposed to N (free of O) at different temps. and the surface phenomena lead to the following results: Co, Ni, Mo, W, Ta, and Si at 700° show no changes. Electrolytic Fe at red heat shows color changes passing into gray as the layer is not of uniform thickness, the layer disintegrating into powder. Mn at red heat may show all colors up to extreme red or it may show no surface change, depending on the original character of the surface. Cr at red heat shows the color changes but slowly. V is yellow at the beginning of red heat and then becomes brown and then copper-colored. Mg and Ca have no color changes but are covered by a gray skin in which the metals melt on higher heat. Ce goes through the colors to the red. The velocity of layer formation on Ce and La in N and in O is given graphically by straight lines when y , the layer thickness, is plotted against $\log t$. For the same sample there may be several intersecting lines, a second line describing the thickening of a second layer after the first layer has scaled off. Another cause of uncertain slope of the straight line curve is the different rates of penetration by the gas through different exposures of the atom grating of the layer. J. M. B.

The quantitative determination of the velocity of filtering. ANNA STEINER. *Kolloid Z.* 31, 204-9(1922).—Some of the properties of hydrated suspensions can be investigated through the detn. of the velocity of filtering with the aid of a special buret. An ordinary Mohr buret provided with a widened portion at its upper end is, through a side tube in the widened portion, connected to a reduced-pressure app. An ordinary or a Büchner funnel passing through a rubber stopper is inserted into the upper widened portion of the buret. An example is given in the detn. of the electrolyte addition which produces the *maximum of flocculation*. A clay suspension is filtered without the addition of electrolyte and with the addition of HCl and of various concns. of FeCl_3 . In tables and curves it is shown that 0.0022 N FeCl_3 produces the same flocculation as 0.025 N FeCl_3 for after a certain time the velocity of filtering becomes the same. The suction applied was 60 cm. Hg. As another example, the differences in commercial CaCO_3 and CaCO_3 pptd. from a hot soln. are given as detd. by the filtering method. The reproducibility of const. results is satisfactory if the time of filtering is not too short. The time factor is regulated by adjusting the suction pressure and the concn. The viscosity of the filtrate also has a decided influence on the velocity of the filtering.

A. MUTSCHALLER

Catalysis of hydrogen peroxide by finely divided platinum. The influence of inhibitors. E. B. MAXTED. *J. Chem. Soc.* 121, 1760-5(1922).—In earlier papers (*C. A.* 15, 1646, 3780) it was shown that the activity of a catalyst for the hydrogenation of an ethylene linkage in the presence of varying concns. of certain inhibitors is a linear function of the concn. of the poison. In the present paper it is shown that the catalysis of H_2O_2 with finely divided Pt in the presence of certain poisons for a wide range is a linear function of the concn. of the poison. With still higher concns. of the poison the extinction of activity is far less abrupt. As poisons HgCl_2 , $\text{Hg}(\text{NO}_2)_2$ and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ were chosen for experiment because their concns. can be regarded as remaining const. throughout an expt. It is suggested that catalyst poisoning may be due to a preferential adsorption of the inhibitor on the surface lattice of the catalyst and preliminary expts. indicate that dil. solns. of the poison metals are strongly adsorbed by Pt catalysts, but that adsorption is incomplete except in the presence of relatively large concns. of catalysts.

JAMES M. BELL

Adsorption and catalysis in fuller's earth. E. K. RIOEAL AND WM. THOMAS. *J. Chem. Soc.* 121, 2119-24(1922).—Fuller's earths from Surrey, Somerset and Florida are not equally efficient in the *bleaching of edible oils*. The relations between the adsorptive and catalytic properties of these earths were examd. to obtain an explanation.

The sp. surfaces were detd. to be in the ratios of 2.35, 2.13 and 1, resp. The adsorptive powers for methylene blue were in the ratios of 2.54, 2.18 and 1. The catalytic actions on H_2O_2 , as measured by the reaction velocity coeffs., were 2.31, 0.58 and 2.51. Color bleaching may consist of both adsorptive and catalytic processes. The iron content of the 3 carths was possibly the governing factor in the catalysis. HENRY C. PARKER

Catalytic agents and chemical equilibrium. J. F. DURAND. *Bull. soc. chim.* 31, 7:9-62(1922); cf. Clarens, *C. A.* 16, 2440.—All of the familiar classical arguments, as well as a few new ones, are presented to prove that equilibria cannot be influenced by catalyzers. J. T. R. ANDREWS

The vapor pressures of solid chlorine and bromine. F. A. HENGLEIN, G. V. ROSENBERG AND H. MUCHLINSKI. *Z. Physik* 11, 1(1922).—Vapor pressures of liquid and solid Cl were detd. between -78° and 142° . An evacuated vessel of known vol. was connected with solid (or liquid) Cl. The quantity of Cl in this vessel was detd. and on assumption of perfect gas law the pressure was calcd. A similar method was used for Br. Between -147° and -153° pressure detns. were made by the quartz-thread manometer of Haber and Kerschbaum (*C. A.* 8, 2642). Values obtained for liquid Cl lie between those of Pellaton (*C. A.* 10, 2167) and Johnson and McIntosh (*C. A.* 3, 2914). The m. p. is calcd. as 170° abs. and other thermodynamic values are given. Values calcd. from the vapor pressure equation as result of Br measurements agree well with Isnardi (*C. A.* 14, 2110). The m. p. of Br is calcd. as -7.3° . By means of the Stern-Tetrode chem. const. of monatomic gases and the dissociation const. of mol. Cl, the vapor pressure of diatomic Cl is calcd. from the theoretical formula for monatomic gases. The chem. const. "of normal state" for diatomic Cl (varying from $+0.06$ to -0.05) is likewise calcd. BENJAMIN S. NEUHAUSEN

The relation between volume and combining capacity. F. EPHRAIM. *Schweiz. Chem. Ztg.* 1920, 360-1.—Complex cations have been shown to be the more stable the larger the spatial extent of the anion (cf. *C. A.* 13, 1285). Polyiodides were studied to det. whether, conversely, complex anions are the more stable the larger the cation. If the spatial extent of the metal nucleus was increased by addn. of a complex, the capacity for formation of polyiodides was increased in the case of ammoniacal solns. of Ni, Cd, Zn, Cu and Co salts, with formation of compds. of the formula $[\text{Me}(\text{NH}_3)_4]\text{I}_x$. If the pptn. of alkaloids depends upon the spatial extent of their cation, this should also be true in the case of the extensive complex cation compds. It was found that alkaloid pptn. reactions were duplicated in the case of cobaltammines. Conversely, reagents which serve for the sepn. of cobaltammines gave the corresponding reactions with alkaloids. $\beta\text{-C}_3\text{H}_7\text{SO}_3\text{H}$ has certain advantages as a pptn. reagent, for it gives very voluminous metal salts which crystallize well, and which can be used for the quant. detn. of some metals. C. C. DAVIS

The theory of freezing mixtures. A. W. PORTER AND R. E. GIBBS. *Phil. Mag.* 44, 787-92(1922).—Expts. and calcs. to show what temp. will be reached by mixing various proportions of ice (I) and salt (S) together at 0° . The 3 cases are considered: no ice remaining, no salt remaining, neither ice nor salt remaining. The euryhydric point will be reached in all cases where S is not less than $1/20(S + I)$ or the quantity of ice is not less than $3/50(S + I)$, assuming both components initially at 0° . To cool a body with thermal capacity θ to -21.6° , the min. quantities will be $\theta/8.4$ g. salt and $\theta/2.8$ g. ice. Practically, somewhat larger quantities are necessary to allow for the formation of dew on exposed surfaces, which is a fairly large factor, as 1 g. dew is equiv. in its heat change to about 8 g. ice. S. C. LIND

Vapor pressures, densities and some derived quantities for ether at low temperatures. R. S. TAYLOR AND L. B. SMITH. *J. Am. Chem. Soc.* 44, 2459-63(1922).—The vapor pressure of Et_2O has been measured between -60° and $+20^\circ$ and the d. between

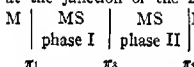
—120° and +70°. From the values obtained and an equation of condition, the latent heats of evapn. and the change in internal energy on evapn. have been calcd. A relation is given connecting the change in internal energy on evapn. and the sp. vol. of the liquid.

H. JERMAIN CREIGHTON

Specific heats of gases with special reference to hydrogen. C. K. INGOLD AND EDITH H. USHERWOOD. *J. Chem. Soc.* **121**, 2286-91(1922).—The complete and complicated formulas for the real and av. sp. heats of H are given; these agree exceedingly well with the observed values over a large range of temp. with an accuracy equal to that of the measurements. For monatomic gases, observed values of sp. heats are accounted for on the theory of equipartition corresponding to 3 degrees of translational freedom. For a diatomic gas, equipartition between 3 degrees of freedom of translation, 2 of rotation, and 1 of vibration together with the potential energy of vibration, must be considered. The sp. heat vs. temp. curve for a diatomic gas must consist of 3 main sections. At low temp. the value $\frac{5}{2}R$ is due to translation only. At intermediate temp. the rotation quantum becomes appreciable and causes C_v to rise to about $\frac{7}{2}R$. At high temp. the vibration quantum also takes effect and brings about a still further rise in C_v . Sp. heat curves have been plotted for H, N, and the halogens and found to follow the above reasoning very closely.

E. F. PERKINS

Potential difference between two liquid phases. E. BAUR. *Z. Elektrochem.* **28**, 421-2(1922).—Aq. solns. of salts, MS, have been shaken with a second non-miscible solvent until the distribution equil. was attained, and the potential difference, π_3 , at the junction of the 2 liquid phases was then measured by means of the chain



the electrode potential differences, π_1 and π_2 , must equal zero, $\pi_3 = \pi_1 + \pi_2$, and $\pi_3 = 0$ when $\pi_1 = \pi_2$. In the expts. the electrolytes (MS) employed were $\text{Hg}_2(\text{NO}_3)_2$, HNO_3 , KNO_3 , and KCl , and the following liquids were used as the second solvent: $\text{C}_6\text{H}_5\text{OH}$, furfural, PrOH , iso-BuOH, AmOH , EtOAc , Et_2O , CHCl_3 and $\text{C}_6\text{H}_5\text{NH}_2$. The results of the potential measurements show that within the limits of exptl. error $\pi_3 = 0$.

H. J. C.

Phosphorus. W. MARCKWALD AND K. HELMHOLZ. *Z. anorg. allgem. Chem.* **124**, 81-104(1922).—With the app. previously described (*C. A.* **15**, 2769) the mean of 33 detns. of the m. p. of violet P is found to be $592.5^\circ \pm 0.5^\circ$ measured with a Pt-PtRh thermocouple. When the rate of heating was $0.25\text{--}0.5^\circ$ per min. the m. p. interval amounted to $0.5\text{--}1.6^\circ$. Contrary to the experience of W. A. Wahl (*C. A.* **7**, 2728), who found a region of critical temp. rather than a definite point, the present authors obtained as a mean of 20 detns. 720.6° , a value 25° higher than the limit observed by Wahl and 45° higher than that calcd. by J. J. van Laar by means of the van der Waal vapor-pressure formula. Violet P on sudden cooling gives white P. According to Ostwald's law, P in a vapor state should condense first as white P. The condensation of red P above 300° is explained by the fact that at that temp. white P changes more or less quickly into red P. White P enclosed in an evacuated tube and heated to $700\text{--}1175^\circ$ when suddenly chilled gives white P and a quantity of violet P in proportion to the temp. to which it was heated. Cooling one end of the tube is more effective than cooling the entire tube. Slow cooling produces pure white P. P vapor at 120 mm. pressure or N_2 satd. with P conducted through a quartz tube at 900° deposits white P mixed with red P, in the first case to the extent of 16%, in the second case, 94%. At first only white P is condensed but the heat conducted from the uncooled part of the tube transforms the white P into red P. Crystals of violet P can sep. from fused violet P only if the fusion contains mols. of violet P. The assumption is made that in the fusion there exists between the mols. of white P and violet P an equil. $nP_v \rightleftharpoons mP_w$, which is dependent on the temp. and in which P,

represents mols. of white P and P_2 mols. of violet P. Above 592.5° the equil. goes completely toward the left, at room temps. toward the right, but its completion is accomplished with an extremely small velocity. If the temp. is just below the m. p. equil. is quickly reached, but with displacement toward the right the further the fusion cools. Fusion causes a soln. of white P supersatd. with violet P from which crystals of the latter sep. Equil. is disturbed and P_2 mols. produced until the whole mass solidifies to violet P. The d_{20} of violet P was found by means of $KPbI_3$ soln. to be 2.36. Violet P crystd. from fusions was found to be identical with Hittorf's phosphorus. By heating to 575° black P was converted to violet P. M. O. LAMAR

Absolute entropy and chemical constants. K. F. HERZFELD. *Ann. Physik* 69, 54-8(1922).—A simple means of getting the classical expression for the entropy from the equations of statistical mechanics is to use as unit of vol. in the generalized space a pseudo-cube of linear dimensions h . This paper is purely mathematical.

R. D. WILLIAMSON

The partition of energy. II. Statistical principles and thermodynamics. C. G. DARWIN AND R. H. FOWLER. *Phil. Mag.* 44, 823-42(1922).—A theoretical paper in 10 sections, including a comparison between the empirical temp. in thermodynamics and the parameter acting as temp. in previous work of D. and F. (C. A. 16, 4102), a critical study of the usual presentation of entropy in statistical theory, a new presentation of entropy closely related to that of classical thermodynamics, a demonstration that, for an assembly in a temp. bath, the present method is equiv. to Gibbs's "canonical ensemble," and an inversion of the method of argument to obtain information about the elementary states from thermodynamic data. S. C. L.

The behavior of solids at low temperatures. WALTHER MEISSNER. *Z. Ver. deut. Ing.* 66, 845-7, 870-8(1922).—A short discussion of the Nernst heat theorem and the Einstein-Debye application of the quantum theory to sp. heats of solids. The expansion, elec. and heat conductivities, the thermolec. and magnetic properties of solids at temps. of liquid H and He are discussed from a theoretical standpoint, and some of the exptl. work of Onnes, Gruneisen, etc., is summarized. BENJAMIN S. NEUHAUSEN

Physical chemistry of the oxides of lead. VI. Anodic behavior of lead and lead dioxide. S. GLASSTONE. *J. Chem. Soc.* 121, 2091-8(1923); cf. C. A. 16, 4111.—Evolution of O at a Pb or a PbO_2 anode takes place at almost the same potentials. This, together with the slow fall of potential on self-discharge in the latter case and the appearance of a black film on the anode in the former, leaves little doubt that the evolution of O at Pb or PbO_2 anodes is due to the intermediate formation of an unstable higher oxide. This oxide is probably present only in very small amts. in solid soln. in the dioxide.

H. JERMAIN CREIGHTON

The chemical and electrochemical behavior of some binary alloy compounds. WILHELM JENGE. *Z. anorg. allgem. Chem.* 118, 105-22(1921).—In chloride, bromide, iodide, nitrate, sulfate, HCl, H_2SO_4 , and NaOH solns., some of the silicides of Ni, Co, and Mn behaved like Si, while others behaved like the metals. Compds. of Sb with Cd and Zn, and of Bi with Tl have almost the same potentials as the base metals. In some cases, the surface of the alloy is rapidly coated over with H. Compds. contg. 0.0-0.475 mol. % Pb with Tl behaved like Tl, and those contg. 0.49-1.00 mol. % Pb behaved like Pb. Alloys of Mg with Cu, Pb, Cd, and Zn were similar to Mg upon first contact with the electrolyte; on further standing the potential decreased rapidly.

W. A. MUDGE

Singular oscillatory movements in mercury electrodes. S. MAGRINI. *Accad. Sci. Med. e Nat. Ferrara* 1921, 1-4; *Sci. Abstracts* 24A, 743-4.—When an Al or Mg wire is brought into contact with a drop of Hg covered by an electrolyte, the Hg begins to undergo rhythmic contraction and distension. These movements continue until

the wire is removed. The rapidity of the oscillations varies with the magnitude of the drop. The phenomenon is particularly marked with an Al wire and a soln. of KCN. Its cause seems to lie in electrolytic polarization and depolarization, with consequent variations in the surface tension of the Hg drop.

D. MACRAE

Conduction of sodium iodide in amyl alcohol at very low concns. C. A. KRAUS AND J. E. BISHOP. *J. Am. Chem. Soc.* **44**, 2206-12(1922).—A method of prepg. AmOH of a very high degree of purity is described. The conduction of solns. of NaI in AmOH at 25° was measured for concns. between 10^{-4} and 17×10^{-4} . The more dil. solns. conform to the mass law. A small but consistent deviation is noted at the higher concns. The value for λ_0 is 11.059.

C. R. PARK

Calibration of cells for conductance measurements. C. A. KRAUS AND H. C. PARKER. *J. Am. Chem. Soc.* **44**, 2422-8(1922).—A critical study of the work of Kohlrausch and his students. Cond. data by Kohlrausch and Holborn do not have sufficient precision for present purposes. The data of Kohlrausch and Maltby are preferable. Directions are given for making up N , 0.1 N , and 0.01 N solns. of KCl by the wt. method. The sp. cond. at 25° of 0.1 N KCl is 0.0128983.

C. R. PARK

The determination of the dielectric constant in the electromagnetic spectrum of undamped oscillations. K. THEODORSCHUCK. *Physik. Z.* **23**, 344-7(1922).—The resonance method with a tube generator is found to be entirely suitable for the measurement of dielec. consts. in the range of long electromagnetic waves and affords a qualitative evaluation of absorption. The dielec. consts. of amyl and isobutyl alcs. (resp., 15.2, and 18.4) do not depend upon wave lengths between 182 and 26 m. Anomalous dispersion at shorter wave lengths has previously been noted by several investigators.

G. L. CLARK

Capillary flow, diffusion, and displacement. LOUIS LUMIÈRE. *Compt. rend.* **174**, 1096-1101(1922).—Whenever a strip of a porous substance is moistened and its upper extremity is folded and submerged in a vessel contg. a liquid, the liquid will siphon slowly through the capillary interstices in thin sheets to the lower extremity, where it will form into droplets. The rate of flow depends largely on the viscosity and surface tension of the liquid, the structure of the fiber, its fineness and degree to which it has been compressed. The rate of flow through each substance tends to become const. for increasing lengths of the lower extremity and beyond certain limits the linear velocity remains const. (3 cm. for blotting paper and 20 cm. for braided cotton). The principal application of this phenomenon lies in the quick and effective washing of precipitates and photographic plates with a minimum amt. of wash water. A plate 9 x 12 cm. was washed free of sol. salts with 30 cc. of water in 15 min., and 25 cc. of ppt. was washed completely in 1½ hrs. with only 50 cc. of water. There are commercial possibilities of application in cases where wash liquor must be used sparingly.

A. R. ALBOUZE

Breath figures. T. J. BAKER. *Phil. Mag.* **44**, 752-65(1922).—Aitken (*Proc. Roy. Soc. Edinburgh* 1893, 94) found that water vapor from the breath deposits differently on a clean polished glass surface after the surface has been traversed by the tip of a flame. In the latter case the deposition is uniform and appears black. Without flame treatment the deposit is white and consists of lens-shaped droplets. Further discussions of the phenomenon appeared in *Nature* from 1911 to 1913. B. has studied the influence of different flames, the transfer of the figures, with or without contact, to a fresh clean plate, and the rendering permanent of them by chem. deposition of Ag which takes place first on the breath figure. HNO_3 and H_2SO_4 have been shown not to be the cause. It is concluded that the flame plays the role of a cleanser removing volatile impurities. A complete theory, especially of the transference, has not yet been offered.

S. C. L.

Variation of the magnetic constant of the oxychromic cation by the action of sul-

furic acid. B. CABRERA AND S. PIÑA. *Anales soc. españ. fis. quim.* 20, 174-81 (1922).—The effect of the addn. of H_2SO_4 to solns. of an oxychromic salt is two-fold and results in a depression followed by an elevation of the magnetic const. In the expts. recorded the variation of the magnetic const. of solns. of an oxychromic salt with time were followed for different values of the ratio H^+/Cr^{+++} . For high values of the ratio the change is so rapid that only the elevation in the magnetic const. is noticeable. For low values of the ratio the initial depression is clearly shown by the exptl. curves. J. C. S.

The drainage error in measurements of viscosity by the capillary tube method. E. C. BINGHAM AND H. L. YOUNG. *J. Ind. Eng. Chem.* 14, 1130 (1922).—As the viscosity of an oil increases, the drainage error increases, dependent upon the time of flow employed. A table of corrections is given for various viscosities or times of flow.

E. C. BINGHAM

The drainage error in the Bingham viscosimeter. W. H. HERSCHEL. *J. Ind. Eng. Chem.* 14, 724 (1922).—Discussion of preceding paper at Birmingham meeting. H. gives a diagram to be used in making drainage corrections. EUGENE C. BINGHAM

Hydrogen as a halogen in metallic hydrides. D. C. BARDWELL. *J. Am. Chem. Soc.* 44, 2499-2504 (1922); cf. *C. A.* 15, 2594.—A new method is described for prep. pure NaH and KH. The fused eutectic mixt. of KCl-LiCl, when properly dried, is a true solvent for alkali hydrides. Upon electrolysis of such a soln. of CaH_2 , H_2 was liberated at the anode in quantity required by Faraday's law.

D. C. B.

Control of gaseous conduction (BUSH, SMITH) 4. The constitution of soap solutions (NORRIS, FALKNER, PRICE) 10.

3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

The search for the ultimate atom. J. L. LAKE. *J. Elisha Mitchell Sci. Soc.* 38, No. 1 and 2, 35 (1922).—Historical review. HENRY W. FASTERWOOD

The structure of atoms according to Bohr's theory. JEAN BARBAUDY. *Technique moderne* 14, 130-1, 179-80, 323-5, 391-2, 436-7 (1922).—A review of the theory and of its consequences. A. P. C.

Periodic structure of atoms and elements. H. N. ALLEN. *Nature* 110, 415 (1922).—By using Crehore's units for at. synthesis (*C. A.* 16, 2634) the elements are built up so that each group has a characteristic structure. F. O. A.

Atoms and electrons. ROBT. N. PEASE. *Nature* 110, 379-80 (1922).—The non-existence of elements of higher at. no. than U and the radioactive instability of the atoms of known elements of highest at. nos. may be accounted for by the large concn. per unit vol. of electrons. Thus Th has 32 more electrons than Ce, but both have face-centered cubic lattices with practically the same distances between at. centers, and hence presumably nearly the same diams. and vols. Similarly in the atoms of U are concd. in about $1/2$ the vol. 32 more electrons than in the atoms of Nd. In such cases there will evidently come times periodically when nos. of electrons in excess of the av. will all be exerting attractive forces on the positive nucleus in the same direction. Then a positively charged constituent of the nucleus might be drawn from its equl. position and because of the repulsive force between it and the nucleus become an α -particle.

G. L. CLARK

The normal helium atom and its relation to the quantum theory. J. H. VAN VLECK. *Phil. Mag.* 44, 842-69 (1922).—An attempt to find a structure for the normal (un-ionized) He atom in harmony with the quantum theory. In part I the present status of the subject and various other attempts are reviewed. It is concluded

that a soln. is not probable without radical reformulation of the quantum hypothesis. Attempts in this direction are also discussed. In part II a soln. is given for the two electrons arranged with axial symmetry, which does not lead, however, to a correct ionization voltage. In part III application is made of quantum conditions to model with axial symmetry and other hypotheses are discussed.

S. C. L.

The radioelements as indicators in chemical researches. FRITZ PANETH. *Z. anorg. Chem.* 35, 549-52(1922).—By adding a small amt. of a radioactive isotope to the substance to be investigated, phenomena not open to ordinary methods of chem. analysis can be detected. Radioelements can be used as indicators: (1) in analytical chemistry to det. the exact soly. of very insol. salts; to investigate the adsorption of traces of substances by ppts., by the filter paper, etc.; to study the properties of rare chem. substances; (2) in electrochemistry to det. whether a mol. is ionized; to det. whether the decompn. voltage is sufficient to deposit on the electrode unweighable quantities of metals; to test the Nernst theory of the exchange between the electrode metal and its ions; (3) in colloid chemistry to distinguish between crystalloids and colloids in dil. solns.; to det. the amt. of surface in absorbing powders; (4) in inorg. preps. to detect the formation of inorg. compds. that are formed only in minimal quantities; (5) in technology for testing the permeability of gummy substances to gases; (6) in physics for experimentally following the so-called "self-diffusion"; the alloying of various metals at low temps.; the soln. velocity of thin layers; the dependence of evapn. velocity on the amt. of evap. liquid; the diffusion of ideal dil. solns., etc.

MARIE FARNSWORTH

The separation of isotopes by distillation and analogous processes. R. S. MULLIKEN. *J. Am. Chem. Soc.* 44, 2387-90(1922); cf. *C. A.* 16, 1359.—The sepn. coeff. is revized from 0.0057 to 0.0083. By means of d. detns. the effect of various factors on the efficiency of sepn. of isotopes by non-equil. distn. has been studied. 50% efficiency is easily obtained, especially in the presence of a film of dirt. The possibility of sepn. non-isotopic liquids by irreversible distn. is pointed out. The failure to sep. isotopes by electrolytic soln. or combination with S is due to the difficulty of obtaining non-equil. conditions at the boundary between two condensed phases.

F. O. A.

The decrease of energy of α -particles on passing through matter. G. H. HENDERSON. *Phil. Mag.* 44, 680-8(1922).—The equation of motion of an α -particle passing through matter is developed, the concepts of resonance and ionization potential being used. The equation gives good agreement with expt. in the case of air but does not furnish a decisive test when compared with other solns. that have been proposed.

S. C. L.

The β -radiation spectrum and its relation to the γ -radiation. LISE MEITNER. *Z. Physik* 11, 35-54(1922).—A continuation of the controversy between M. and Ellis (cf. *C. A.* 16, 2071, 3030, 3434) as to the relation between β -radiation and γ -radiation. Further exptl. results are presented proving that for Th B and Ra D only one L level, that known as L_{α} , exists in the excitation of the characteristic radiation arising from the γ -radiation coming from the nucleus.

W. F. MCGGERS

The adsorption of uranium X and its isotope, thorium, by basic ferric acetate. A. C. BROWN. *J. Chem. Soc.* 121, 1736-43(1922).—B. finds Freundlich's adsorption equation $x/m = ac^{1/n}$ to hold if $1/n = 1$. For values less than 1 the law is approx. The results seem to be in agreement with Langmuir's theoretical deductions on the adsorption of gases at a surface. Solns. contg. U X alone and U X with Th were used.

L. D. ROBERTS

Depth of penetration of recoil atoms into copper and nickel. ERNST RIE. *Sitzb. Akad. Wiss. Wien.* 130, IIa, 293-9(1921).—Thin layers of Cu of known depth were deposited upon Pt electrolytically. The plates were charged negatively and exposed to Ra Em. The activity was measured before and after the electrolytic plate was re-

moved by dil. HNO_3 . The av. depth of penetration was found to be approx. 10μ , in fair accord with Wertenstein's value of 20μ . The values reported by Godlewski (cf. *C. A.* 11, 1789) were shown to be too large. Only 40% of the activity on pure Pt plate could be dissolved by HNO_3 .
D. C. BARDWELL

Further studies in the electron theory of solids. The compressibility of a bivalent metal and of the diamond. J. J. THOMSON. *Phil. Mag.* 44, 657-79(1922).—By using a method previously developed (*C. A.* 16, 2257) the compressibility has been calcd. of metallic Ca and of the diamond. The results of the calcn. are in good agreement with expts. of Richards. The subject of *metallic cond.* is then considered in the light of the electron theory of solids. Three types of solids are distinguished: (a) Arrangement of atoms in one lattice system, electrons in another coordinated system in which each electron has no closer connection with any particular atom than with several others. This type includes the metals and elements like B and C (in the form of diamond) which are nonconductors. (b) A type represented by the salts, where the atoms are arranged in lattices but each electron has much closer relation to a particular atom than to any other; each atom is supposed to have lost or gained one or more electrons from the neighboring oppositely charged atom. (c) A type where the lattices are built up of non-electrified units, each electron remaining attached to a particular atom. The property of cond. or insulation as exhibited by type (a) atoms is then considered and a theory is developed according to which electrons lying along a line of a lattice may travel along that line carrying energy and electricity and having a sufficiently long period of vibration to absorb a whole quantum of energy. The theory is elaborated that *elec. and thermal cond.* are due to the movement of such chains and is shown to account for the variation of elec. resistance with temp., for the super-cond. of metals at very low temp. and for Wiedemann and Franz's law of the proportionality between elec. and thermal cond.

S. C. LIND

Impactionization by low-speed positive hydrogen ions in hydrogen. A. J. SEXTON. *Phil. Mag.* 44, 809-23(1922).—An exptl. examn. of the ionization of H_2 by impact of H ions formed by electronic collision. The results indicate that the crit. voltage is the same as for ionization by electrons. Ionization was observed in a field as low as 18 v. The efficiency of H ions in producing ionization is much less than that of electrons under similar conditions.
S. C. L.

An electron theory of electric conduction in metals. E. H. HALL. *Proc. Nat. Acad. Sci.* 8, 307-13(1922).—This paper is a modification and extension of the dual conception of conduction previously advanced by H. (*C. A.* 14, 3352; 15, 1248) and is set forth in a series of 24 propositions
MARIE FARNSWORTH

The thermal ionization of gaseous elements at high temperatures. A confirmation of the Saha theory. A. A. NOYES AND H. A. WILSON. *Proc. Nat. Acad. Sci.* 8, 303-7 (1922).—The investigations of Arrhenius and the more recent researches of Wilson on the elec. cond. of flames into which salt sols. are sprayed indicate that the conduction arises from an ionization process of the type $M = M^+ + E^-$. The way in which the conductance changes with the concn. makes it possible to calc. the relative values of the ionization constns. K of the five alkali metals. The approx. abs. values of these constns. can be found by combining with the conductance data the mobility of the electrons and the no. of them per cc. in similar flames free from salt. These constns. correspond well with those calcd. from the ionization potentials of the metals by the thermodynamic equation employed by Saha (*C. A.* 15, 468, 799, 1452) and are a striking confirmation of his theory.
MARIE FARNSWORTH

The emission of electrons by X-rays. G. SHEARER. *Phil. Mag.* 44, 793-808 (1922).—Expts. undertaken to establish the relation between the no. of electrons emitted by X-rays from metals and the at. no. of the metal. The exptl. method consists in allow-

ing a beam of X-rays from a Coolidge tube with W target to pass through a hemispherical glass window and to impinge upon one side of a hollow brass cube covered with the metal under examn. The cube is suspended in an evacuated chamber by a wire leading to a string electrometer by means of which the rate of charging due to electron emission is detd. Electrons emitted by the window are arrested by a magnet before entering the chamber. It was found necessary to differentiate between the high- and low-speed electrons. The effect of the latter was eliminated by imposing a low opposed voltage sufficient to prevent their emission. The residual effect is due to the high-speed electrons. The metals examd. were Al, Fe, Ni, Cu, Ag, Sn, Au, Pb, Bi. The swift electron emission was found proportional to the at. no. (N) as expressed by: $n' = k(N-a)$, where n' is the no. emitted, and k and a are consts. The value of a is approx. 10. It is to be remembered that n' is the number escaping, not that liberated from the atom. Approx. calcn. shows that the number liberated is proportional to $A(N-10)$, where A is the at. wt. Results for the compds. As_2O_3 , KI and RbI showed the emission to be greater than expected if additive for the two elements concerned. Special (characteristic) electron emission was found to be practically absent for Cu and Sn under varying voltage. Selective emission in the direction of the elec. vector could also not be detected. The electron emission for unit intensity (n) was found to diminish with increasing voltage (V), and $nV^{1/2}$ was approx. const. The low-speed emission was found to be a secondary effect of the high-speed electrons and may be regarded as an ionization phenomenon similar to Δ -ray production by α -rays. S. C. LIND

The dependence of the discharge upon the out-gassed condition of the electrodes. ALEX. JANITZKY. *Z. Physik* 11, 22-30(1922).—Certain X-ray tube targets became inactive after continued use. On exposing to the air, pumping out and sealing off their activity returned for a brief period. Expts. were then made which showed that the inactivity of the targets to serve as anodes was due to their out-gassed condition. Further out-gassing renders them unable to act even as cathodes. This is the true explanation of the "polarization" of X-ray tubes observed by Ratner (*C. A.* 16, 1043). F. O. A.

The tungsten X-ray spectrum with a mica spectrometer. USABURO YOSHIDA AND SHINSUKE TANAKA. *Mem. Coll. Sci. Kyoto Imp. Univ.* 5, 173-8(1922).—The L-series X-ray spectrum of W is investigated photographically with a bent mica spectrometer. A sheet of mica 0.06 mm. thick was fastened on the surface of a wood cylinder. The grating const. was 9.858 Å. All the prominent lines were found to be visible up to the 5th order and the line 1.095 Å., for example, to the 10th order, besides many weak lines. Fair agreement in wave lengths with those detd. by others was obtained but 11 new lines of unknown origin were also detected. These may be due to reflection from cylindrical mica. G. L. CLARK

Atomic light. K. FOESTERLING. *Z. Physik* 10, 387-92(1922).—The assumption of a spherical wave for light and of Bohr's principle of correspondence requires the further assumption of a new form of energy in the atom because of Stark's expts. (*C. A.* 10, 849), which prove a continuous emission of energy from electrons to the ether. F. O. A.

Influences of the presence of gases or vapors upon the intensities of the lines of the secondary spectrum of hydrogen. MASAMICHI KIMURA AND MITSU HARU FUKUDA. *Mem. Coll. Sci. Kyoto Imp. Univ.* 5, 153-63(1921).—A study was made of the effect of pressure on the intensities of the lines of the secondary spectrum of H. For this purpose Geissler tubes contg. a lump of pure Na satd. with H were excited by an induction coil giving a 30-cm. spark. The pressure of the gas within the tube was varied by heating the Na. The spectra were photographed with a 2-prism spectrograph. It was found that certain lines in the secondary spectrum became enhanced while others were weak-

ened as the pressure within the tube was increased. Tabulation of these lines reveals the fact that many of the enhanced lines belong to Fulcher's group II, to which belong lines enhanced with increasing voltage; while the lines weakened with increase of pressure belong almost entirely to Fulcher's group I, which comprises lines unaffected by changes in voltage. The addn. of the vapors of H_2O , Hg , Br , I , Cl and S to the H within the tube had the same effect on the distribution of intensities in the secondary spectrum as was observed for changes in pressure of the tubes contg. H alone. C. C. KIESS

Note on the intensities of the lines of the Balmer series of hydrogen. MASAMICHI KIMURA AND MITSU HARU FUKUDA. *Mem. Coll. Sci. Kyoto Imp. Univ.* 5, 165-8 (1921).—The spectra of various tubes contg. pure H and HI , HCl , Hg , S and Na at pressures of $1/2$, 3, 7, 10 and 14 mm. were photographed with a small const. deviation spectrograph. It was found that up to pressures of 7 mm. the ratios of the intensities of the Balmer lines remained unaffected. At 10 mm. and higher pressures, however, the presence of the vapors of other elements caused the higher members of the Balmer series to diminish in intensity as compared with $II\alpha$. C. C. KIESS

The variability of spectra. T. R. MERTON. *Engineering* 113, 332-4 (1922).—The radiation emitted by an element in the state of a luminous gas varies with the exptl. conditions, the mode of excitation and also the presence of other elements. Examples are given of variations in flame spectra and the spectra of gases in elec. discharge tubes. Special attention is given to changes in the spectra of H when water vapor or He is present and similar changes in the He spectrum produced by traces of C . W. F. M.

Formation of fume ions in electrical precipitation (NIWA) 4. Interpretation of light-sensitivity in photography (SVEDBERG) 5. Cyanine dyes (VI). Dyes containing a quinoline and a benzothiazole nucleus. The thioisocyanines (BRAUNHOLTZ, MILLS) 10. Control of gaseous conduction (BUSH, SMITH) 4. Film for X-ray photography (Brit. pat. 184,519) 5. Separating Tl and radioactive metals from Pb ores and making white lead pigment (Can. pat. 225,160) 26. Röntgen-ray apparatus (Brit. pat. 184,485) 18.

4—ELECTROCHEMISTRY

COLIN G. FINK

Paul Martyn Lincoln. ANON. *Elec. World* 80, 1140 (1922); 1 illus.—Biographical sketch. C. G. F.

The electrochemical industries. CHARLES BLANCHET. *Rev. ing. index techn.* 29, 11-6, 51-62 (1921); *France-Belgique* 1, 118-28, 189-98, 255-66, 318-31 (1922).—A review of the methods used in electrothermic and electrolytic industries, with a brief mention of the production of ozone. A. P.-C.

Electrical research viewed as a career. WILLIAM SPARAGEN. *Elec. World* 80, 1102-3 (1922).—S. briefly outlines the vast field and possibilities of research, the necessary qualifications and the compensation. "We have an abundant supply of men who are willing to conduct expts., but there are few who generalize or deduce fundamental laws from expts." C. G. F.

The age of producing pure metals electrochemically. ANON. *J. four elec.* 31, 106 (1922).—A short review. C. G. F.

Electric furnaces produce quality steel. J. A. MATHEWS. *Elec. World* 80, 1086, 1088, 1091 (1922); 6 illus.—The reasons for the world-wide expansion of elec. steel making are (1) cheapening of wholesale power rates, (2) extreme flexibility and adaptability of furnace, and (3) superior quality of product. For installed elec. furnace capacity, Italy now ranks ahead of Germany, England and France, and second only to the U. S. C. G. F.

Electric furnaces for the melting of steel. K. P. GRIGOROVITCH. *Rev. metal.* 19, Abs. Sec., 412-13 (1922).—A review of the resistance (Hoskins), the induction (Rodenhauser), and the arc (Rennerfeld and Heroult) types of elec. furnaces and their industrial applications. W. A. MUDGE

Status of electric furnaces. L. H. KNAPP. *Elec. World* 80, 605-7 (1922); 9 illus.—A review. C. G. F.

Electric heat, its generation, propagation and application to industrial processes. E. F. COLLINS. *Trans. Am. Electrochem. Soc.* 42, preprint (1922).—The development of elec. heat by passage of current through solid resistors, through liquid and through gaseous media is discussed at length, reference being made in particular to the fundamental theoretical principles. An efficient, com. elec. heating app. must be constructed with due regard to chem. reactions taking place, to the effect of mech. changes, such as expansion with heat, to phys. factors such as heat transmission and heat emissivity and to the comparative cost and operating factors. C. G. F.

When to use acid- and basic-lined furnaces. F. H. SWEET. *Elec. World* 80, 993-9 (1922).—Acid operation is preferable (1) when the P and S in the scrap arc and will remain less than the P and the S required in casting; (2) when the C and Si can vary widely; (3) when low power consumption and high rate of operation are of prime importance; (4) when close phys. tests are not required; and (5) when very small castings only are made. Basic lining is best (1) when the S in the scrap is above the limits specified for the product (2) when the steel must be made to close C, Si and Mn analysis; (3) when close or good phys. tests must be met; (4) when alloy steels are to be made; (5) where steady load is essential; and (6) when refining of cast iron is to be considered.

W. H. BOYNTON

Manufacture of carbon disulfide. G. A. RICHTER. *Trans. Am. Electrochem. Soc.* 42, preprint (1922).—A new plant for the manuf. of CS_2 . The furnace consists of a refractory lined cast iron shell. A resistance bed of broken arc light carbon is distributed between the electrodes. Charcoal and liquid S are periodically fed into the furnace. Detailed thermal data are submitted indicating that the process is operating comparatively efficiently. Heat of formation of 1 kg. CS_2 320 cal., loss due to drying charcoal 5 cal., loss of heat due to subliming of part of S 97 cal., radiation losses 610 cal.; total heat, supplied electrically, 1,032 cal. or 1 kg. CS_2 requires 1.20 kw.-hr. Also in *Chem. Met. Eng.* 27, 833-41 (1922). C. G. F.

Plant for electrolysis of alkaline chlorides. G. QUAINK. *Chem.-Ztg.* 46, 489-90 (1922).—This is a description of the *Billiter-Siemens* cell as applied to German practice in the manuf. of NaOH and Cl. Much is claimed for the efficiency and low cost of operation, but little data are given from which to judge the results obtained. The voltage given, 3.7 to 4.0 v., is substantially higher than that in electrolytic plants operating in U. S. Two cuts are shown which indicate a large floor space required.

L. D. VORCE

Experiments on the ferrous-calcium chloride solution for the electrodeposition of iron. W. E. HUGHES. *Brass World* 18, 261-5, 283-9 (1922).—The soln. consisted of: $FeCl_2$ 6 lbs. (2.7 kg.), $CaCl_2$ 6 $\frac{1}{2}$ lbs., (3.06 kg.), and water 1 gal. (3.8 l.), which makes about 2 gals. (7.57 l.) of soln. $CaCl_2$ is dissolved in the water, the $FeCl_2$ added and the soln. filtered or allowed to settle and then siphoned. The expts. were conducted: to det. the general working conditions and the nature of the deposit, to ascertain the effect of altering the soln. to det. the max. c. d. and temp. usable and to test the adherence of the deposit to the base metal. C. d. limits were wide. At temps. of 90-100° the c. d. may reach 240 amp./sq. ft. while at room temp. the soln. is not workable. The best conditions are a temp. 90-110°, a c. d. of 120 amp./sq. ft., and sp. gr. of soln. 1.45. The e. m. f. is 0.7-1.0 v. Under favorable conditions the deposit is light gray in color, finely

cryst., even in thickness, rounded on the edges, and has few pits or lumps, and is somewhat malleable. Agitation of the soln. or cathode movement are without advantage. Electrically deposited Fe adheres in a manner similar to Ni to a similar base and withstands rough machine treatment. H. concludes that revisions are necessary in several of our laws of electromagnetism and states that "a current-carrying circuit will tend to produce any and only such motions of its conductors as will produce a counter e. m. f. somewhere in that circuit, though not necessarily in the moving part itself."

W. H. BOYNTON

The forms of electrodeposited iron and the effect of acid upon its structure. I. Deposits from the chloride bath. W. E. HUGHES. *Trans. Faraday Soc.* 17, 442-5 (1922); cf. following abstr.—The soln. for the exptl. work consisted of FeCl_2 56% and CaCl_2 anhyd. 5 lbs. (2.27 kg.). The sp. gr. of the soln. is 1.375 and it is used in a rectangular wrought-iron tank, lined with asbestos board. The anodes were sheet steel and the cathode was a short length of solid Cu rod, highly polished and carefully cleaned. The FeCl_2 was reduced to FeCl_3 by HCl and the passage of a heavy current through the bath between sheet-iron electrodes. Expts. show the effect of acidity on the deposit, the microstructure, the conditions of formation of the principal deposit, the correlation of conditions of deposition and structure, and the types of structure of electrodeposited Fe. The effect of acid upon the structure is to prevent the formation of the normal structure—the structure obtained is fibrous. Structures found in iron deposits formed in chloride baths are varieties of the two general and distinct types, and the type obtained depends upon the prevailing set of conditions during the deposition. The fibrous type is formed in agitated solns. as well as in acid solns. Macroscopic features correspond to definite microscopic structure, enabling the depositor to control the process more effectively. Three photomicrographs are shown.

W. H. BOYNTON

Electrodeposition of iron. W. E. HUGHES. Dept. Sci. Ind. Research (London), *Bull.* 6, 50 pp. (1922); 63 illus.—The structure of a no. of samples of Fe deposited from the $\text{CaCl}_2 + \text{FeCl}_2$ soln. (see abstracts above) are described and microphotographs shown. H. concludes that the formation of cryst. deposits of Fe and Cu by electrodeposition is essentially in no way different from crystn. from rock magmas, molten metals or salt solns. The dominant factor governing the structure of the crystd. substances is in all cases concn. of mols. or atoms, other factors of deposition such as temp., c. d., etc., being contributors. High concn. (at the surface of the cathode) gives rise to small grain size, low concn., to large grain size.

C. G. F.

The early days of the lightning arrester. F. SCHROTTKE. *Elektrotech. Z.* 43, 1250-60 (1922).—Historical note.

C. G. F.

Small oil engine battery charging sets. W. WILSON. *Beama* 11, 723-30, 811-18 (1922).

C. G. F.

Formation of fume ions in electrical precipitation. II. Y. NIWA. *Inst. Elec. Eng. (Japan)* No. 402, 47-54 (1922).—Assuming the fume particle and the ion to be conducting spheres N. derives a theory of formation of fume ions. When the charges on the particle and on the ion are of equal sign, the energy of the system has a max. value at a certain distance, within which the ion is attracted to the particle. However when the charges are opposite, there is always an attractive force between them, but this force predominates effectively within a definite distance. These effective distances decrease with the increase of the ratio of the charge on the particle to that on the ion for the former case and increase for the latter. The larger the charge on the particle becomes, the more difficult it is for the particle to attract the similarly charged ions, while the easier it is to attract the oppositely charged ions. Finally, when the rates of the recombination of similarly and oppositely charged ions to the particle are equal, the charge on the particle assumes a definite value and cannot increase further. N. the-

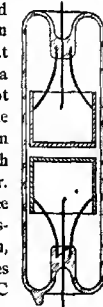
oretically calcs. their quant. relation and calcs. that the charge on the particle can be represented by $\frac{1}{2} \times n'v'/nv$ times the charge on the ion, where n, n' and v, v' are, resp., the numbers of ions per unit vol. and the relative velocities of ions and particles. To keep the charge on the particle large this ratio should be increased as far as possible; and unless the ratio of densities of both kinds of ions be greater than two (assuming equal relative velocities) the charge on the particle cannot be definite. From this standpoint N. discusses the charge and motion of the particles in the space between 2 parallel plate electrodes and shows theoretically the reason why the pptn. efficiency of the treator of a parallel plate type is inferior to that of the cylindrical type. He also criticizes the expts. of Hauer (*C. A.* 14, 3016) from his point of view. When the temp. of gas rises, the kinetic energy of the ion increases, and if this energy becomes so large as to permit the free motion of the ions against the attractive force between the particle and the ion, the formation of fume ions becomes much limited. This temp. is calcd. to be very much higher (about 3000°) than may be attained in engineering work. In the formation of fume ions where the particles are not conducting the limiting temp. is in the range attainable. Certain kinds of dust treated by elec. pptn. are not conducting. In this case, however, the moisture and the other impurities adhering to the surface of the dust are sufficient to give some cond. It is natural that such kinds of cond. should be easily affected by a small change of temp. and other gas conditions. N. discusses the pptn. efficiency, the gas cond. and properties of particles, and finally concludes that the high temp. of the gas and the low cond. of the particles hinder the formation of fume ions and lower the pptn. efficiency. N. shows that these conclusions agree well with the working data of the pptn. treator for 180,000 cu. ft. of the gas per min. at the Asio smelter, Japan.

L. D. VORCE

The quantitative analysis of the thermionic tube oscillation generator. H. G. MOELLER. *Electrician* 89, 537-8(1922).

C. G. F.

Control of gaseous conduction. V. BUSH AND C. G. SMITH. *J. Am. Inst. Elec. Eng.* 41, 627-35(1922).—In devices depending on gaseous conduction for their operation much higher voltages can be employed if these devices are so constructed that all paths available for discharge are short. E. g., the construction shown in the diagram, with clean electrodes 1 mm. apart and pure He at a pressure of 2 mm., will withstand continuously 10,000 v. and pass a current which is hardly measurable. With a construction similar except that one of the electrodes is in the form of a hollow cylinder with a hole opposite the center of the other electrode the gaseous discharge can then take place only within the central region where there are long paths. Such a discharge is remote from the glass of the tube or any other insulator. It is thus not affected by parasitic charges and is steady in accordance with circuit conditions. A study of the *clean up of gases* in the elec. discharge has shown that when the hollow electrode contains molten Sn, the gas driven into the Sn as gaseous ions is re-liberated in small bubbles during the operation of the tube. It has also been noted that with C electrodes no disappearance of the working gas takes place provided the gas is chemically inactive and the C of the proper grade. Making use of the above principles a magnetically controlled tube (rectifier or amplifier) and a hollow cathode rectifier have been constructed.



D. MACRAE

Use of high-power vacuum tubes. IRVING LANGMUIR. *Elec. World* 80, 881-3 (1922).—A 20-kw. 3-electrode vacuum tube has been developed and manufactured in relatively large numbers. The anode consists of a Cu cylinder which forms a portion of the envelope of the tube and is cooled by contact with running water. The filament is W, 1 mm. in diam. and is heated by a current of 50 amps. at about 20 v. A 100-kw.

tube of nearly the same type is now being developed. A tube of the magnetron type has been constructed to supply 1000 kw. of 20,000 cycle power with an anode voltage of 20,000 v., d. c. By employing a "thoriated" W filament under very special conditions, the energy loss in heating the filament can be reduced to 0.1 of that necessary with a pure W cathode. The advantage of the thoriated filament is due to an adsorbed film of metallic Th on the surface of the filament. As the Th evaps. it is supplied by diffusion from the interior of the filament. The presence of gases which would oxidize the Th is avoided by the use of the vapors of Mg, or the alkali metals. Substances contg. C have also been used.

D. MACRAE

Dielectric loss and breakdown. J. B. WHITEHEAD. *Elec. World* 80, 1049(1922).—W. discusses the problem of accounting for the behavior of the composite insulating materials used in practice, when subjected to a. c. voltage. C. C. VAN VOORHIS

The electrical units. J. WALLOT. *Elektrotechn. Z.* 43, 1329-33(1922).—W. suggests greater simplification and rationalization of the units in use at present. C. G. F.

Extinguishing generator fires (SOREN) 13.

Galvanic batteries. A. DRYIN. *Brit.* 184,658, July 8, 1921. Addition to 14,119 (C. A. 9, 3178), 1914. Charged negative electrodes of storage batteries are dried by passing a stream of non-oxidizing gas through a closed chamber contg. the electrodes. The gas is circulated continuously by means of a pump and is heated by means of hot H₂O or steam passing through heaters combined with the chamber. Condensers are used for removing steam from the gas. Gases such as N, A, He, H, CO, and illuminating gas may be used.

Galvanic batteries. C. G. SMITH. *Brit.* 184,049, June 30, 1921. A storage cell is filled with plaster of Paris to absorb the electrolyte and to sep. and support the electrodes. In one method of construction the cell is filled with plaster of Paris and H₂O into which greased glass, etc., plates are pressed to form pockets for the electrodes. The plates are removed when the plaster has set. The electrodes may be of the lead grid type or each pocket may be provided with a lead conductor surrounded with a paste of H₂SO₄ and Pb₂O₄ or PbO with a small quantity of powd. Al₂(SO₄)₃. The Al₂(SO₄)₃ may constitute about 2% of the vol. of the Pb oxides. The Provisional Specification states that the ends and bottom of each pocket may be lined with a lead strip of such length that when the pocket is filled with active material one end of the lead strip may be bent over to close the top of the pocket and be joined to the other end of the strip and to a terminal bar. Cf. 7619, 1889.

Grids for storage batteries. R. S. HALLETT. *Can.* 225,587, Nov. 7, 1922. The grid is provided with insulated corners.

Electrolytic cells. D. REICHNSTEIN. *Brit.* 183,455, July 17, 1922. To increase and render more const. the detector effect of electrolytic cells an oxidizing agent such as chromic acid is added to the electrolyte.

Electrolytic cells. E. A. LESUEUR. *Can.* 224,095, Sept. 26, 1922. An anode for electrolytic cells has a conducting stem protected by a conducting sheath of resistant metal and several sheets of resistant metal electrically connected with the latter and extending laterally in both directions. Cf. C. A. 16, 3817.

Couplings for electrolytic cells. WM. G. ALLAN. *Can.* 225,540, Oct. 31, 1922.

Electrodes and electrolytic batteries. A. T. STUART. *Can.* 225,661, Nov. 7, 1922. A bi-polar battery for H and O generation has a pair of opposed current distributors with a gap between them, means for passing an elec. current across the gap and metallic strips arranged in series within the gap with their major planes arranged in the direction of the flow of the current between the distributors.

Accumulator electrodes. O. NEUMANN and A. NEUMANN. Brit. 184,762, Nov. 23, 1921. Electrodes are made from an alloy contg. Sn. Na and Hg may also be added, and the cathodes may contain Sb. In an example the anodes consist of Pb 70 parts, Sn 5, Na 8, Hg 12, and Zn 5; the cathodes of Pb 60, Sn 5, Na 8, Hg 12, Zn 5, and Sb 10. The paste with which the grids are filled contains Li_2O ; the anodes may also contain MnO_2 . These substances are mixed with PbO , preferably lead orange obtained by roasting PbCO_3 . The cathode material may also contain the sulfates of Zn, Hg, Na, and Li, together with Pb acetate; the anode material may contain the sulfates of Mn, Li, Hg, and Na, with Pb(OAc)_2 . A soln. of sodium phenolate or lecithin may be used as a binding medium. The electrodes are formed in a soln. of Na_2SO_4 and Li_2SO_4 acidified with H_2SO_4 , and the electrolyte consists of a soln. of the sulfates of Zn, Hg, Na, and Li, together with KMnO_4 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$, the soln. being acidified with H_2SO_4 .

Electrolytic refining of tin. A. E. WHITE. Brit. 183,507, Feb. 24, 1921. In refining impure Sn with an electrolyte contg. H_2SiF_6 , an agent such as one of the phenols or their homologs or benzene is added to enable coherent deposits to be obtained from a soln. contg. less than 6%. The electrolyte may be prepd. by passing current through an impure Sn anode and a soln. contg. 5.5% of H_2SiF_6 , 5% of H_2SO_4 , and 0.3% of cresol, the impure commercial form of which is preferred. A little glue may be added. Cf. 11,818, 1915 (C. A. 11, 236).

Electrolytic decomposition of alkali salts. M. WILDERMAN. Brit. 184,938, June 16, 1921. In a large cell having a no. of Hg cathodes for the decompn. of alkali salts, means are provided for preventing or diminishing the flow of current between the cathodes and the walls of the vessels or between one cathode and another so as to prevent oxidation of the Hg or formation of solid amalgam.

Electrolytic manufacture of potassium bicarbonate. CHEMISCHE FABRIK GRIESH-EM-ELEKTRON and R. SUCHY. Brit. 184,244, May 2, 1921. Normal K_2CO_3 is formed in the cathode compartment of a cell contg. a soln. of KCl and KHCO_3 . The cathode liquid is withdrawn. KCl is added to replace that consumed, and CO_2 is then introduced to ppt. KHCO_3 . The liquid, thus restored to its original compn., is returned to the cell.

Cementation. CAMMELL, LAIRD & CO., LTD., J. M. ALLAN, A. P. HAGUE and T. MIDDLETON. Brit. 184,920, June 7, 1921. Ferrous articles are carburized by immersing them in a bath of fused metallic salts contg. combined C and making them the cathode of an electrolytic circuit. A suitable bath consists principally of carbonate of soda with or without the addn. up to 25% of the whole of carbonate of Ba or of other alkalis or alk. earths. When high C concn. is required, Na nitrite or other fusible N-yielding salt up to 5% of the whole is added. The bath container may be made of a Ni-chrome-Fe alloy and may be used as the anode of the circuit or a sep. anode consisting of a rod plate, ring or tube of C, Fe or steel may be used. The c. d. used is from 0.5–2 amp. per sq. in. of cathode surface. Articles may be decarburized by immersion in a bath which has been recently used for the carburizing process described.

Method of discharging oscillatory currents. E. F. NORTHRUP. Can. 225,102, Oct. 24, 1922. The oscillation current is passed through two oppositely placed gaps between Hg and a solid electrode in series in a closed container in the presence of a non-carbonizable gas.

Discharge gap. E. F. NORTHRUP. Can. 225,103, Dec. 24, 1922. The gap specified is from Hg to a solid electrode in the presence of a gas other than air. The gap is also shown in combination with other elements for operating synthetic processes.

Electromagnetic apparatus. WESTERN ELECTRIC CO. Brit. 184,804, Aug. 16, 1922. In electromagnetic app., such as polarized bells, electromagnets, relays, telephone receivers, and measuring instruments, having open magnetic circuits, the cores or armatures, or both, are formed of a magnetic material having a higher permeability than

Fe at low magnetizing forces and including in its compn. two of the following metals: Mn, Fe, Ni, Co, and Cu. An alloy contg. Fe 21.5% and Ni 78.5% and an alloy contg. Ni 55, Fe 34, and Cr 11% are given as examples of suitable magnetic material.

Thermionic valves. WESTERN ELEC. CO., LTD. Brit. 185,030, Sept. 9, 1921. One or more of the electrodes, preferably the grid or anode, or both, are provided with a black coating of NiO to increase heat radiation. The coating may be produced by heating a Ni electrode in air or O₂ in an elec. furnace, to a temp. of 900°. A coating of NiO or MoO₃, or other semi-insulating substance, on the grid prevents secondary emission of electrons therefrom, owing to the presence of particles from the filament cathode. The coating may be removed from the anode over a part which lies in the path of the electron stream, by means of a jet of H or other reducing agent while the surface of the anode is heated, or by means of a blast of abrasive material.

Vacuum tubes. NAAMLOOZE VENNOOTSCHAP PHILIPS' GLOEILAMPENFABRIKEN. Brit. 185,410, Aug. 28, 1922. In a gas-filled glow discharge tube, the electrodes are formed of, or covered with, a metal such as Hg, Cd, or Cs which when disintegrated has little or no tendency to stick to the glass walls at ordinary temps.

Tungsten powder; tungsten compounds. NAAMLOOZE VENNOOTSCHAP PHILIPS' GLOEILAMPENFABRIKEN. Brit. 183,816, July 14, 1922. W powder suitable for the production of lamp filaments is obtained by reducing in H materials called "complex tungstic acids." The materials mentioned are compds. of tungstic acid with silicic and boric acid, resp., and are prepd. by boiling Na₂WO₄ with water glass and HOAc or with silicic acid; or boiling tungstic acid and NH₃ with silicic acid; or by boiling Na₂WO₄ with boric acid. In each case the treatment is continued until strong HCl does not ppt. tungstic acid. The reaction mixt. is in some cases poured into strong HCl and an oily layer is sepd. from which the complex tungsten acid is crystd. Cf. 155,851.

Incandescent filaments. G. R. FONDA. Can. 225,458, Oct. 31, 1922. A filament consisting of a solid soln. of B in W has a lower vapor pressure at high temp. than W, a lower temp. coeff. of resistance than W not contg. B and at elevated temp. a sp. resistance substantially equal to W not contg. B.

5—PHOTOGRAPHY

LOUIS DERR

Interpretation of light-sensitivity in photography. T. SVEDBERG. *Phot. J.* 62, 310-20 (1922).—The Einstein law of photochem. equiv. is that the light-energy required to decompose 1 mol. is always $Nh\nu$, where N is the Avogadro const. 6×10^{23} , h the Planck const. 6.56×10^{-27} , and ν the light-frequency; or, that the photochem. decompn. of a mol. requires the energy of a light-quantum $h\nu$ and no more; but as secondary and purely chem. reactions det. the light-sensitivity of a substance in most cases, the law frequently fails. A distinction is made between plate-sensitiveness, which is the quantity of immediate practical interest, grain-sensitiveness, which is largely a matter of statistics as to grain-size, and sensitiveness of the halide material of the grain. Larger grains are demonstrably more sensitive than smaller ones. Even if radiation-density is uniform throughout the vol. of the grain, the developability is detd. entirely by the surface layer. If there is more than one developable center in a single grain, reduction proceeds merely from these several centers instead of one. The sensitivity of the Ag halide material is therefore measured by the no. of developable centers per sq. cm. of grain surface, and there are great differences between emulsions in this respect, even after the factor of grain size is eliminated. There is therefore no necessary inconsistency in the demand for highly sensitive emulsions of fine grain. L. DERR

Sensitometry of photographic emulsions and a survey of the characteristics of

plates and films of American manufacture. R. DAVIS AND F. M. WALTERS, JR. *Bur. Standards, Sci. Paper No. 439*, 120 pp. (1922).—This deals with the speed, development, color sensitiveness, filter factors, scale, and resolving power of about 90 U. S. brands of plates and films. A calibrated Mazda C lamp was used as the source of light, with special blue filter to approximate daylight. Exposures were made through a sector disk, and development was at const. temp. Many spectrograms and curves are given. No names of plates or makers are mentioned. L. DERR

Removing emulsion from plates. F. LIMMER. *Chem.-Zig.* 46, 651-2 (1922).— NH_4F in 1-2% soln. is recommended as rapid, effective, and altogether the best stripping agent. It is not suitable for use with films and papers. L. DERR

Reducibility of the individual halide grains in a photographic emulsion. T. SVEDBERG. *Phot. J.* 62, 183-6 (1922).—Photomicrographs of AgBr grains before and after development show that even over a distance as small as 1μ no noticeable transfer of Ag takes place from the unaffected to the developable grain. Apparently a grain is completely reducible or is not reducible at all. L. DERR

Relation between sensitiveness and size of grain in photographic emulsions. S. E. SHEPPARD AND A. P. H. TRIVELLI. *Phot. J.* 61, 400-3 (1921). Research Lab. Comm. No. 138, Eastman Kodak Co.—Though there is no necessary connection between grain-size and light-sensitiveness, it is considered that a probability relation exists, whereby grains of larger size or greater projective area have a probability of acquiring a given reactivity which varies with projective area. Evidence is given indicating that reduction of the grain is preceded by adsorption, and takes place as a breakdown of the adsorptive complex of Ag halide and reducing agent, this being initiated or accelerated by the latent image as Ag nucleus. If this view is correct, the equil. need not be identical with that in aq. soln. Also, the catalytic effect of Ag nuclei probably depends decisively upon their position relative to a given array of atoms in the Ag halide lattice. A final modifying factor is grain-aggregation in relation to the reduction potential of the developer. For low values of this, developability will not be transferred from exposed to unexposed grain; for high reducing energy, infection of contiguous grains appears very probable. II. T. SVEDBERG. *Phot. J.* 62, 186-96 (1922); cf. *C. A.* 15, 2393.—A given Ag halide grain will be developable if it contains one developable center or more, and if the centers are distributed haphazard not all grains will become developable. The av. no. of centers per grain, as found by expt., agrees with the no. as calcd. by the laws of chance, and the no. increases rapidly with increasing size of grain. Partially developed grains show the position of the centers and the no. in single grains. Though not demonstrated, it appears that in exposure to X-rays the absorption in the grain is so small that the centers are distributed uniformly throughout the grain, while for light the absorption is so great that the centers are formed only at the surface on the exposed side. Recent detns. of the relation between grain-size and percentage-developable grains apparently show only slight penetration of the developer into the grain, so that the reducibility should depend on the occurrence of at least one center in the surface layer. L. DERR

Svedberg's method of grain analysis of photographic emulsions. S. E. SHEPPARD AND A. P. H. TRIVELLI. *Phot. J.* 62, 196-7 (1922); cf. *C. A.* 16, 391.—The study of sources of possible error leads to the conclusion that the procedure provides a valuable and reliable method of optical analysis when due precautions are taken. L. DERR

New desensitizers. R. E. CROWTHER. *Brit. J. Phot.* 69, 351-3 (1922); cf. *C. A.* 16, 1914, 2644.—Pinakryptol soln. 1:5000 reduces the speed of super-speed portrait film to 0.009 of the original value, about the same as phenosafranine; pinakryptol green 1:5000 reduces it to 0.006. Neither pinakryptol nor pinakryptol green affects the latent image harmfully. L. DERR

Direct positive films for amateur cinematography. K. D. B. FIRM. *Bull. soc. franç. phot.* [3] 9, 261-5(1922).—Ordinary negative film is unsuitable for transformation into a direct positive; film such as is used for printing positives, and of uniform thickness of emulsion, is necessary. Development of the exposed film is best done in a bath of water 1 l., pyrocatechol (Poulenc étoile B) 10 g., Na_2SO_4 cryst. 50 g., anhyd. K_2CO_3 100 g., KBr 1 g. Development must be carried to almost complete opacity of image. The bath may be used repeatedly. After development and a short wash, the Ag image is removed by a bath of water 1 l., KMnO_4 2 g., H_2SO_4 (66° Bé.) 5 cc. This removal is best done in bright yellow light and must be thorough. The KMnO_4 is eliminated by a 3-min. immersion in 5% NaHSO_5 , and this is followed by redevelopment in white light, either the preceding developer or metol or metol-hydroquinone being used. A 10-min. wash completes the process.

L. DERR

Gelatin in the photographic process. S. E. SHEPPARD. *J. Ind. Eng. Chem.* 14, 1025-32(1922).—In the prepn. of the AgBr emulsion important factors are the freedom of the gelatin from desensitizing impurities, the relative content of jelling protein and non-jelling hydrolyzates, the viscosity of its sols and their setting points. The factors governing viscosity are discussed. Sensitiveness is largely controlled by inhibitory substances in the gelatin. The mechanical strength of the jelly phase and swelling capacity are important. The isoelect. point and the H-ion concn., especially with the acid fixing and hardening bath, are important for the behavior of the ampholytic gelatin. The behavior of gelatin jellies on drying is considered explicable without recourse to structure theories of the jelly.

L. DERR

Halation preventives with desensitizing dyes. H. MEISSNER. *Phot. Rundschau* 59, 233-4(1922).—Phenosafranin is dissolved in zapon varnish thinned with its bulk of amyl acetate, a little sugar is added and the mixt. coated on the back of the plate. In the developing bath enough dye is dissolved to permit completing development in white light, and halation is suppressed.

L. DERR

Action of soluble chlorides and bromides on reduction with ammonium persulfate. S. E. SHEPPARD. *Phot. J.* 62, 321-33(1922). Comm. No. 140, Research Lab. Eastman Kodak Co.—Tables and curves, for which the original paper must be consulted, are given showing the differential reduction by $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The effects of acids and halides were measured. Lippo-Cramer's colloid or "dispersoid" theory is favored, rather than the catalytic theory. Higson's results on $\text{K}_2\text{S}_2\text{O}_8$ in general agree with S.'s for $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The acceleration by acids and the mechanism of the reaction are discussed.

L. DERR

Mutual infection of contiguous silver halide grains in the photographic emulsion. A. P. H. TRIVELLI, F. L. RICHTER AND S. E. SHEPPARD. *Phot. J.* 62, 407-10(1922).—In emulsions having nearly spherical grains, of small range of sizes, there is little or no transfer of developability from one grain to another; in emulsions having a wide range of grain sizes and many polyhedral tablets, mutual infection plays a large part in detg. the speed and density with increase of exposure.

L. DERR

Silver and halogen determination in photographic preparations. E. LEHMANN. *Z. angew. Chem.* 35, 373-4(1922).—Ordinary analytical methods fail because of the difficulty of sepg. the halide mixts. from the vehicle and the support. The emulsion may be removed from glass plates by 5% HCl followed by cold Na_2CO_3 in satd. soln. A mixt. of 20% CH_3COOH and 4% HNO_3 destroys the gelatin and the Ag is recoverable by heating, free from org. matter. To det. Ag in papers, thorough development, washing, and holling in HNO_3 are preferred. For halogen detn. Bekk's modification of Barbigny's method (cf. C. A. 9, 2042) is preferred. Bonino's method (cf. C. A. 16, 1053) was not used. For difficult papers the removal of the halogens as alkali compds. is the only practicable method. Reduction is accomplished by 5% caustic alk. hydroxylamine

sulfate, 75 cc. water answering for 500 cm.² paper. Other methods are described.

L. DERR

Recent contributions of chemistry to photography. S. E. SHEPPARD. *J. Ind. Eng. Chem.* 14, 820-3(1922).—A review, accompanied by an extensive bibliography.

L. DERR

Chloranol. LUMIÈRE AND JOUGLA. *Phot. Korr.* 68, 26(1921).—This is the name given to a developing agent prepd. by equimol. combination of methyl-*p*-aminophenol and chlorohydroquinone. It is analogous to metoquinone.

L. DERR

Chemical and physical development. A. STEIGMANN. *Phot. Ind.* 1921, 550-2.—Phys. development is characterized by requiring many nuclei on which the Ag can deposit, while in chem. development the nuclei act as catalysts for the reduction of the AgBr grains. Supersatn. with Ag occurs in both cases, but in chem. development it is restricted to the immediate proximity of the AgBr grains, while with phys. development it may occur anywhere in the film. The discussion includes the color changes of Ag sols in the swelling of gelatin, explained by supposing that in the swelling the smaller colloidal particles are more or less uncovered by the larger particles previously shielding them, thus giving to the color an admixture of red.

L. DERR

The synthesis of phenosafranine. C. H. HALL, JR. *Maryland Acad. Sci. Bull.* 2, 68(1922).—The details for the various stages in the synthesis of this photographic sensitizer have been taken from standard works. The reactions involved are: (A) $\text{PhNH}_2 \rightarrow \text{PhNHN}_2\text{Ph} \rightarrow \text{NH}_2\text{C}_6\text{H}_4\text{N}_2\text{Ph} \rightarrow$ (B) $p\text{-(MH}_2)_2\text{C}_6\text{H}_4$, and the joint oxidation of (A) and (B) with $\text{K}_2\text{Cr}_2\text{O}_7$.

G. W. STRATTON

Capillary flow, diffusion and displacement (washing photographic plates) (LUMIÈRE) 2.

Color photography. E. A. LAGE. *Brit.* 183,189, March 19, 1921. A composite plate is prepd. for indirect three-color photography by separately prep. 3 Ag halide emulsion films, sensitized for the different spectral divisions, and superposing them directly upon each other and pressing them into optical contact by expressing the intervening air. Light-filters may be applied to the back of the films. A glass plate coated with a red-sensitive emulsion layer is wetted at the edge all round and a film sensitized for yellow, green, and blue rays is superposed, emulsion side upwards, in contact with the emulsion on the glass and pressed into contact by yielding rubber rollers. Another film sensitized for blue only is similarly superposed on the second film. The filter layer on the back of the films is preferably in the form of an easily washed out layer of colored gelatin. The films are sepd. for development by cutting round the edges.

Photochemical printing surfaces. E. DOBLKE. *Brit.* 183,817, July 15, 1922. A layer of natural or artificial resin sensitized, *e. g.*, with a chromate, is exposed under a negative until the portions exposed are rendered insol. in a developer comprizing (1) an alkali or a substance having an alk. reaction, or (2) alc. or other org. solvent, with or without the addition of alk. substances. The light-sensitiveness of the layer may be increased by adding thereto (1) CS_2 , either pure or contg. S, or (2) albumin decomn. products. Numerous examples of resins, sensitizers and developers are given.

Film for X-ray photography. N. E. LUBOSHEV. *Brit.* 184,519, March 2, 1921. The base or support of a film for X-ray photography is made of a material such as gelatin, glue, gum, celluloid, or collodion, in which is incorporated throughout the depth a salt or sofn. used in the prepn. of intensifying screens, such as Ca tungstate or Ba cyanoplatinate. The base may be coated on one or both sides with emulsion.

Photographic stencils. M. J. D. CARTER. *Brit.* 183,923, April 30, 1921. In the process for producing photographic stencils for use with water-ink duplicators, dental

or yoshino paper, silk, or other thin and open fabric, before being coated with sensitized gelatin or albumin, are coated with varnish to render the stencils waterproof. A thin layer of gelatin mixed with $\frac{1}{4}$ its wt. of $K_2Cr_2O_7$ or a similar layer of albumin and $(NH_4)_2Cr_2O_7$ is applied to one side of the varnished sheet and dried in a dark room. The sheet is exposed under a positive in sunlight, and developed in cold or lukewarm water, which dissolves out the unexposed gelatin or albumin. The varnish thus exposed is then removed by treatment with a solvent, such as methylated spirit, in such a way as to leave the covered varnish intact.

Cinematographic film. A. F. M. Orr. Brit. 184,495, March 10, 1921. A protective coating for a cinematographic film is produced by applying a soln. contg. colloidal, Et_2O , methylated spirit, and either HCO_2H , $AcOH$, or $AcOEt$, and allowing to dry.

6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

The rare earths. A. DAMIENS. *Bull. sci. pharmacol.* 29, 449-58(1922).—A general discussion.

F. S. HAMMETT

Germanium hydride. FRITZ PANETH AND E. SCHMIDT-HEBBEL. *Ber.* 55B, 2615-22(1922).—Although having only about 0.2 g. Ge at disposal, P. and S. were able to det. the ratio H:Ge. Mean of 5 detns. = 4.008; 3.94-4.08. Various of the methods previously used by P. in the prepn. of metal hydrides were tried; best results were obtained by addn. of Zn or, better, redistd. Mg to H_2SO_4 soln. of Ge. Absence of germanes, analogous to higher boranes and silanes, was made nearly certain. By an indirect method the no. of H atoms in the mol. could be calcd. from the stoichiometric data. The no. approached 4 as the purity of the hydride increased; 34%, 2.1; 81%, 3.53; 84%, 3.55; 90%, 3.85; 95%, 3.99. The color of Ge rings deposited in a Marsh tube is variable and depends in high degree on the surface of the glass or quartz and on the nature of the accompanying gas. A black, a red and a yellow ring may be deposited at a small distance from each other. Identification can be based on the fact that no other hydride deposits so strongly colored rings; in doubtful cases heating in O_2 to form white GeO_2 , which on heating in H_2 forms copper-colored Ge sol. in $NaClO$, may be used. As is completely volatilized in the O_2 . GeH_4 is remarkably stable. It is not decompd. by 50% KOH or P_2O_5 . Marsh tubes should be heated in several places for safety. This stability should render easy prepn. of pure hydride when 1 g. of metal is available.

A. R. MIDDLETON

Lead-acetate complexes. R. WEINLAND AND R. STROH. *Ber.* 55B, 2210-25(1922); cf. *C. A.* 15, 3596.—Methods of prepn. and analysis of the following salts are described. $[Pb_2(AcO)_2](ClO_4)_2 \cdot H_2O$; $[Pb_2(AcO)_2]ClO_4 \cdot 2H_2O$; $[Pb_4(AcO)_4](ClO_4)_3 \cdot 2H_2O$; $[Pb_3(AcO)_3]ClO_4 \cdot AcO$; $[Pb_3(AcO)_3](NO_3)_2 \cdot H_2O$; $[Pb_2(AcO)_2]NO_3 \cdot H_2O$. All these salts crystd., some exceptionally well. The perchlorates explode on strong heating or percussion.

A. R. M.

Constitution of basic lead salts. R. WEINLAND AND R. STROH. *Ber.* 55B, 2706-18(1922).—Marignac's basic perchlorate (I) and a new one (II) prepd. by the authors were both found by cond. measurements to give 3 ions in aq. soln. On the basis of Werner's views as to the constitution of basic salts (*C. A.* 2, 636) they should be formulated

lated $\left[Pb \begin{array}{c} \diagup OH \\ \diagdown OH \end{array} Pb \right] (ClO_4)_2 \cdot 1.5H_2O$ and $\left[Pb \begin{array}{c} \diagup OH \\ \diagdown OH \end{array} Pb \right]_2 (ClO_4)_2$. The perchlorate

residues in both could be replaced. By treating the aq. soln. of I with the appropriate alkali salt were obtained chloride, nitrate, dithionate and nitroprusside with cation

unchanged; ferri- and cobaltcyanide yielded dust-like, homogeneous ppts. with changed cation: $Pb_4(OH)_2Fe(CN)_6(CIO_4)_2$ and $Pb_4(OH)_2Co(CN)_6(CIO_4)_2$. From II were obtained similarly with cation unchanged the chloride, iodide, nitrate and dithionate; but chromate formed the cation of I, $Pb_5(OH)_7CrO_4$, and the following salts of more complex cations were obtained: with little and with more ferricyanide, $Pb_5(OH)_8Fe(CN)_6(CIO_4)_3$ and $Pb_5(OH)_7Fe(CN)_6 \cdot 3.5H_2O$, also $Pb_5(OH)_8Co(CN)_6(CIO_4)_3$ and $Pb_5(OH)_8FeNO(CN)_6 \cdot CIO_4 \cdot H_2O$. The same methods applied to $Pb(AcO)_2$ showed that it also contains the same di-ol cation, as it gave the same chloride and dithionate as I and the especially well characterized compds., $Pb_5(OH)_7Fe(CN)_6(AcO)_2 \cdot H_2O$, from concd. soln.; $Pb_4(OH)_2Fe(CN)_6$, (A) dark yellow amorphous ppt. from dil. soln., soon going over into fine, granite-red crystals; $Pb_4(OH)_2Co(CN)_6$, and $Pb_5(AcO)_8Fe(CN)_6 \cdot 2H_2O$ by treating A with dil. AcOH. The following salts were so stable as to be recrystd. from water: $Pb(AcO)_2NaClO_4$; $(Pb(AcO)_2)_2NaClO_4 \cdot 3H_2O$; $(PbOHCIO_4)_2NaClO_4 \cdot 3H_2O$. They are to be further investigated. The neutral acetato perchlorates and nitrates (preceding abstr.) differ from the basic salts only in having acetate in place of the bridging OH groups. The combined results indicate that aq. and AcOH solns. of $Pb(AcO)_2$ contain the acetates of at least four polynuclear cations. In more dil. solns. hydroxo-acetato cations probably occur. Methods of prepn. and analysis are detailed for all the salts mentioned.

A. R. M.

Existence of sulfur tetroxide. I. F. MEYER, G. BAILLEUL, AND G. HENKEL. *Ber. 55B*, 2923-9(1922).—The work of Berthelot (*Compt. rend.* 86, 20, 288(1878)) upon S_2O_7 was repeated, with a flowing gas mixt. instead of an enclosed mixt. Contrary to B. the product had no appreciable vapor p. at 0° and less than 0.01 mm. at 20°. It remained unchanged for a short time when removed from the discharge app., then suddenly puffed up with formation of a thick white cloud. A strongly oxidizing acid remained. The substance dissolved only very slowly in much water. Analysis showed more O than corresponds to S_2O_7 . A new discharge tube (pictured) was devised suitable for analytical weighing, capable of maintaining high vacuum and permitting analyses in vacuum. About 25 expts. were made with this tube. The ratio $SO_2:2SO_3$ was the highest attained. From these merely preliminary expts. it is concluded that the anhydride of Caro's acid, $(SO_3)_2$, is present in a mixt. of several products.

A. R. M.

The sodium tungstates. I. E. F. SMITH. *J. Am. Chem. Soc.* 44, 2027-36(1922).—A study of the Na tungstates has shown that the 4:10 salt (A) represents a very definite series among these salts. Forcher's method leads to the formation of A and not to the 5:12 salt. HCO_2H acting on normal Na tungstate gives only A. The 9:22 salt is a mixt. of A and the 5:12 salt. The crysals of A effloresce rapidly in dry air and upon resolu. in H_2O evolve considerable heat; 19 parts dissolve in 100 of H_2O at room temp.; their d. is 4.3. The m. ps. of the various salts are as follows: $Na_2O \cdot WO_3 \cdot 2H_2O$ 655°; $5Na_2O \cdot 12WO_3 \cdot 28H_2O$ 705.8°; $4Na_2O \cdot 10WO_3 \cdot 23H_2O$ (A) 680.8°; $9Na_2O \cdot 22WO_3 \cdot 51H_2O$ 683.3°; $Na_2O \cdot 4WO_3 \cdot 10H_2O$ 706.6°. The behavior of A with a large no. of inorg. and org. salts is briefly described. Its compn. is confirmed by that of the following salts, prepd. by adding an excess of the resp. chloride to A in boiling H_2O , which all have the compn. $4M \cdot O \cdot 10WO_3 \cdot xH_2O$: Calcium (25 H_2O), white granular powder; barium (22 H_2O); strontium (26 H_2O); nickel (34 H_2O); greenish white; cobalt (35 H_2O), pink; manganese (30 H_2O). Na paratungstate at 100° loses 21 of its 28 mols. of H_2O ; the remaining 7 mols. (H_2O of constitution) are probably combined in the form of H_2WO_4 and the formula of the salt may well be written $(5Na_2O \cdot 5WO_3 \cdot 7H_2O \cdot 7WO_3) \cdot 21H_2O$, indicating that the substance is an acid salt. Similarly $Na_2O \cdot 4WO_3 \cdot 10H_2O$ loses 7 H_2O at 100°, $BaO \cdot 4WO_3 \cdot 9H_2O$ loses 6 and A loses 17 of its 23 mols., indicating that it, too, is an acid salt. This was confirmed by titration with 0.1 N Na_2CO_3 and Me orange and by cond. detns., $Ba(OH)_2$ being used to neutralize the acid present; the break in the cond. curve corresponded with the results given above.

C. A. R.

Some new lecture experiments with hydronitric acid and the trinitrides. A. W. BROWNE AND A. B. HOEL. *J. Am. Chem. Soc.* **44**, 2116-19(1922).—Four lecture table expts. are given which illustrate the similarity in behavior of HN_3 and its salts, and H_2O_2 and the alkali peroxides. J. T. R. ANDREWS

Autoreduction of sulfurous acid. G. M. BENNETT. *J. Chem. Soc.* **121**, 1794-5 (1922).— H_2SO_3 liberated from its salts at 100-120° may undergo instantaneous autoreduction with production of H_2S . Thus when powdered Na_2SO_3 or $\text{Na}_2\text{S}_2\text{O}_3$ or their satd. solns. are dropped into 60-70% H_2SO_4 , H_2S is evolved. The reaction is assumed to be $4\text{H}_2\text{SO}_3 = \text{H}_2\text{S} + 3\text{H}_2\text{SO}_4$; it may be an intermediate stage in the liberation of free S which has been frequently observed. Negative results were obtained with gaseous SO_2 , its satd. solns. or the solid hydrate. The high reducing power of H_2SO_3 may be due to the momentary existence of the unsymmetrical acid $\text{H}_2\text{SO}_2\text{OH}$. JAMES M. BELL

The properties and structure of pernitric acid. Iw. TRIFONOW. *Z. anorg. allgem. Chem.* **124**, 123-35(1922).—For raw materials the following solns. were used: (a) 3% H_2O_2 , (b) 3% NaNO_2 , (c) 3.75% KNO_2 . These concns. give, according to Raschig (*C. A.* **2**, 636), the max. effect. PhNH_2 is a more sensitive and more expedient reagent for HNO_3 than KBr. Neither great diln. nor cooling is necessary for the formation of HNO_4 ; it can easily be detected in acidified solns. of H_2O_2 -nitrite of considerable concn. Below 70° such a mixt. is not completely decomposed; above 70° it breaks down rapidly. In strongly concd. solns. HNO_4 may be detected 2.5 hrs. after acidification of the H_2O_2 -nitrite mixt. In dil. soln. it is rapidly hydrolyzed. If the nitrite is in great excess over the H_2O_2 , the former reduces the HNO_4 , which can be detected only in the nascent state in case the oxidation product of the reagent is not decolorized by the excess nitrite. HNO_4 in acidified H_2O_2 -nitrite mixtures can be detd. accurately by adding excess KBr, dilg. 10 fold, followed by KI soln. and titration of the liberated I. By following quant. the formation of HNO_4 with different ratios of the reacting substances T. is led to an equation different from Raschig's, and to the formula $\text{N}_2\text{O}_4 \cdot n\text{H}_2\text{O}$. The acid oxidizes C_6H_6 to $o\text{-NO}_2\text{C}_6\text{H}_4\text{OH}$; pyridine and naphthalene analogously. Alk. is oxidized by the nascent acid to acetone. PhNO_2 and pernitric acid soln. give an intense yellow color in aq. soln. which is feebly converted to orange by alkalis. M. O. LAMAR

Properties of pure hydrogen peroxide. III. O. MAASS AND W. H. HATCHER. *J. Am. Chem. Soc.* **44**, 2472-80(1922).— H_2O_2 is diamagnetic, having a susceptibility of 8.8×10^{-7} . The soly. of H_2O_2 in various org. solvents has been measured. The dissoc. of NaCl , NaNO_3 and Na_2SO_4 in H_2O_2 is of the same order as in H_2O . The tendency towards the formation of mol. compds. with H_2O_2 is less than in H_2O , there being evidence of only one such compd., $\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2$. The action of the H halides on H_2O_2 and the soly. of the halogens and NH_3 in this liquid have been studied. With NH_3 a cryst. compd., $\text{NH}_2\text{H}_2\text{O}_2$, is formed. The stability of this compd. shows that it is the OH-ion which causes the decompn. of H_2O_2 . H. JERMAIN CREIGHTON

Carbon suboxide. ERWIN OTT. *Umshau* **26**, 576-8(1922).—The compd. C_3O_2 , originally prepd. by Diels and Wolf (*Ber.* **39**, 689(1906)) from malonic acid and P_2O_5 , is obtained purer and in much greater yields from tartaric acid and Ac_2O . G. L. C.

Reactions between gaseous oxides of nitrogen and alkaline solutions. A. SANFOURCHE. *Compt. rend.* **175**, 469-72(1922).—Data are submitted which show that absorption in caustic solns. invariably gives more nitrate and less nitrite than in H_2SO_4 . If there be deficiency of alkali at any local point, water acts to form HNO_3 and NO which is reoxidized in presence of excess O_2 but remains unaltered in its absence. Any oxides which escape absorption in passing through the soln. react as above with water vapor in the gaseous phase. This is made visible by the fog of HNO_3 and the deposit on the walls of the absorption vessel of an acid dew in spite of the excess of alkali below. Analyses are vitiated because this vesicular acid is difficult to retain. H_2SO_4 should be substituted for alk. absorbents in analysis of gaseous N oxides. A. R. MIDDLETON

Residual affinity and coordination. IX. Cobaltamine salts of the nitro dyes. G. T. MORGAN AND H. J. S. KING. *J. Chem. Soc.* 121, 1723-9(1922); cf. C. A. 15, 2414; 16, 1366.—To det. whether the substantive nitro dyes furnish chelate groups when combined with cobaltamines, 4 typical dyes were examd., viz., picric acid, dipicrylamine, 2,4-dinitro- α -naphthol and 2,4-dinitro- α -naphthol-7-sulfonic acid. Unlike the mordant dyes of the quinone oxime, alizarin and hydroxyazo series, the substantive nitro dyes do not furnish chelate groups each capable of reacting as two associating units in the coordination sphere of Co. The following compds. were prepd.: chloropentamminocobaltic picrate, reddish brown needles; aquopentamminocobaltic picrate, small, yellow needles; hexamminocobaltic picrate, sulfur-yellow needles. All are sparingly sol. in cold water and partially hydrolyzed on warming. The salts of dipicrylamine were red, amorphous solids, more sol. in cold water than the others: the chloropentammino, aquopentammino and hexammino salts were prepd. Chloropentamminocobaltic 2,4-dinitro- α -naphthoxide, $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{C}_{10}\text{H}_6\text{O}_2\text{N}_2)_2 \cdot 3.5\text{H}_2\text{O}$; also the aquopentammino (1.5H₂O) and hexammino (1.75H₂O) salts, identical in color, being orange when wet and brick-red when dry, pasty amorphous ppts. very sparingly sol. in cold water. Chloropentamminocobaltic 2,4-dinitro- α -naphthoxide-7-sulfonate, $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{C}_{10}\text{H}_4\text{O}_6\text{N}_2\text{S})_2 \cdot 3\text{H}_2\text{O}$, small, orange needles; hexammino salt, $[\text{Co}(\text{NH}_3)_6](\text{C}_{10}\text{H}_4\text{O}_6\text{N}_2\text{S})_2 \cdot 6\text{H}_2\text{O}$, bright yellow, irregular plates. A. R. MIDDLETON

Spontaneous decomposition of ammonium chlorate. FRED FAIRBROTHER. *J. Am. Chem. Soc.* 44, 2419-22(1922).—The cold satd. soln. appears to undergo no decomposition when kept indefinitely. If any solid phase is present, decompn. becomes evident in a few days and may become violent if much solid phase is present. The rate of decompn. is autocatalytically accelerated when the products are not quickly removed. The course of decompn. is probably very slow autooxidation with formation of HNO₃, N₂, Cl₂ and H₂O; HNO₃ then reacts with more chlorate, forming HClO₄ and ClO₂, which rapidly oxidize NH₄ with formation of more HNO₃ and Cl₂. Perchlorate does not appear to be formed. The relative amts. of the products vary with the conditions. The solid residue is NH₄NO₃ with no chloride. A. R. MIDDLETON

Intermetallic actions. The system aluminium-arsenic. Q. A. MANSURI. *J. Chem. Soc.* 121, 2272-7(1922).—Al and As combine to form the compd. Al₃As₂ as shown by thermal and chem. analysis. The action commences at about 750° where yellow As is formed and reacts with the Al. The brown compd. Al₃As₂ is stable at high temp. and its m. p. is above 1600°. It evolves AsH₃ when exposed to moisture. When heated in air, alumina and As₂O₃ are formed. J. A. ALMQUIST

7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

Electrometric titrations. A. LASSIGNOR. *Bull. soc. chim.* 31, 817-31(1922).—A lecture describing the principles involved in electrometric titrations, the reactions that have been studied in this way, the method of carrying out the work and the necessary app. W. T. H.

Bimetallic electrode systems in electrometric analysis. I. Systems comprising two dissimilar metals. H. H. WILLARD AND F. FENWICK. *J. Am. Chem. Soc.* 44, 2504-15(1922).—In the past, 3 electrode systems have been used in electrometric analysis: (1) an unattacking metal electrode and a const. half-cell, usually a calomel electrode; (2) instead of the calomel electrode, a compensation electrode of which the potential is equal to that of the unattacking electrode at the end of the titration; (3) the half-cell is a soln. of the same compn. as that of the titrated soln. at the end pt. The numerous expts. here described show that the half-cell of the electrometric titration

app. may be replaced by a metal (other than pure Pt or Pd) or alloy of the Pt group and by W. The end pt. obtained with such a bimetallic system differs from that usually obtained but it is unchanged in location and not only is the app. somewhat simplified but there is often a marked gain in distinctiveness of the end pt. II. Theory of bimetallic systems: systems comprizing two similar metals. *Ibid* 2516-9.—Two theories have been advanced for the cause of the existence of an e. m. f. between the ions of an oxidizing agent and an insol. electrode. LeBlanc imagined an actual interchange of charges, or electrons, between electrode and electrolyte. Nernst, on the other hand, considered the e. m. f. to be due to an O charge at the electrode in the case of an oxidizing agent and to a H charge in the case of a reducing agent. According to this conception, which is in agreement with the ionic theory and Faraday's law, the insol. electrode functions as a gas electrode. A series of expts. was planned to see if the correctness of such an assumption could be proved and as a result of these expts., the conclusion is drawn that the e. m. f. of systems comprizing 2 insol. electrodes is due merely to a difference in the solvent power of the 2 metals for gas. In a monometallic electrode system, the change in e. m. f. is that of a true oxidation potential and changes continuously but shows a marked change at the end-pt. With a bimetallic system, practically all the change in e. m. f. is confined to within less than 0.05 cc. of the end pt. The actual magnitude of the sudden change is normally less but, as compared with the preceding change, it is relatively greater, so that the sharpness of the end pt. is increased, causing a more rapid and more accurate titration in most cases. On the other hand, it is somewhat more difficult to anticipate the end pt.

W. T. H.

The electrometric determination of end-points. E. MÜLLER. *Z. angew. Chem.* 35, 563-6 (1922).—A lecture describing (1) what is meant by an electrometric potential, (2) to what extent this e. m. f. can be used for detg. the end point of a reaction, (3) how the end point is actually found and (4) what special reactions have been found suitable for electrometric titration.

W. T. H.

The electrometric standardization of titanous solutions. W. S. HENDRIXSON AND L. M. VERBECK. *J. Am. Chem. Soc.* 44, 2382-7 (1922).—Satisfactory results were obtained in standardizing $Ti_2(SO_4)_3$ solns. against $KMnO_4$ or $K_2Cr_2O_7$ and detg. the end-pt. electrometrically. The results were practically the same when the Ti^{+++} soln. was run into an excess of Fe^{+++} soln. and the excess titrated with permanganate or dichromate, as when the Ti^{+++} was added directly to a known vol. of standard permanganate or dichromate.

W. T. H.

The effect of alkali on the titration of certain metals with ferrocyanide. W. D. TREADWELL AND D. CHERVET. *Helvetica chim. acta* 5, 633-9 (1922).—The compn. of the ppt. and the sharpness of the end pt. in the titration of Cd^{++} , Fe^{++} and Pb^{++} with $[Fe(CN)_6]^{4-}$ is influenced by the nature of the alkali cations present. To account for this effect, it is suggested that the at. vol. has considerable to do with the giving up of free energy. In titrating $CdSO_4$ soln. with $K_4[Fe(CN)_6]$ a ppt. corresponding to $K_2Cd[Fe(CN)_6]$ was obtained only in very dil. solns. At higher concns. of Cd, the ppt. was enriched with this element. If $RbCl$ was added to the soln. a better end pt. was obtained electrometrically and contained exactly 1 Cd to 1 $[Fe(CN)_6]$. The addition of Cs^+ resulted in an even sharper end pt. When $Na_4[Fe(CN)_6]$ was used for the titration, the end pt. was less satisfactory and the ppt. was $Cd_2[Fe(CN)_6]$. The at. vols. of the elements in question are indicated by Bragg's estn. of at. diams. in 10^{-7} mm. (cf. *C. A.* 14, 3584). Thus, Bragg found: Li 3.00, Na 3.55, K 4.15, Rb 4.50, Cs 4.75, Ag 3.55, Ti 4.50, Be 2.30, Mg 2.85, Ca 3.40, Sr 3.90, Ba 4.20, Zn 2.65, Cu 2.75, Ni 2.70, Co 2.75, Fe 2.80, Mn 2.95, Cd 3.20, Pb 3.80. In titrating Zn^{++} with $K_4[Fe(CN)_6]$ the end pt. was reached when all the Zn was pptd. as $K_2Zn_2[Fe(CN)_6]$. When the titration was made with $Na_4[Fe(CN)_6]$, the ppt. was $Zn_2[Fe(CN)_6]$ but if KCl was added to

the soln. the ppt. was $K_2Zn_3[Fe(CN)_6]_2$ again. If a little Cs_2CO_3 soln. was added, the ppt. became of the type $Na_2Zn[Fe(CN)_6]$. In titrating Pb, the ppt. with $K_4[Fe(CN)_6]$ was $Pb_2[Fe(CN)_6]_3$; a little RbCl soln. had no effect but addition of 1 milli-mole of CsCl caused a ppt. of the type $K_2Pb_2[Fe(CN)_6]$. W. T. H.

Reductions with cadmium in volumetric analysis. II. W. D. TREADWELL. *Helvetica chim. acta* 5, 732-43(1922).—1. *Titration of uranium*. When a UO_4^{++} salt is reduced in a Cd reductor (cf. C. A. 15, 3041) some tervalent U is formed but this exposed to air undergoes so rapid an oxidation to the quadrivalent state that an electrometric titration can be accomplished with permanganate on the basis of the equation: $5 U^{+++} + 2 MnO_4^- + 2 H_2O = 5 UO_4^{++} + 2 Mn^{++} + 4 H^+$. The results appear to be better when Cd, rather than Zn, is used in the reductor and when the reduced soln. is caught in an open beaker rather than in a flask contg. CO_2 . 2. *Titration of titanium in the presence of iron*. After passing through a Cd reductor the Ti is reduced to the tervalent condition and can be titrated with $KMnO_4$, or better $FeCl_3$ soln., when the end pt. is detd. electrometrically. It is well to add a little NaF to the soln. If the Ti content is very low as compared to the Fe content, it is probably advisable to reduce the Fe by H_2SO_4 , add NH_4OH and filter off the ppt. of H_2TiO_3 contaminated with $Fe(OH)_3$. The ppt. can then be dissolved in H_2SO_4 , reduced with Cd and titrated with $FeCl_3$. 3. *Titration of vanadium*. HVO_3 in acid soln. is reduced by Cd to V^{++} . If the reduced soln. is collected in a flask filled with CO_2 accurate results are obtained by an electrometric titration with $KMnO_4$. $5 V^{++} + 3 MnO_4^- + 3 H_2O \longrightarrow 5 HVO_3 + 3 Mn^{++} + H^+$. 4. *Titration of indigo*. If a sample of indigo is dissolved in concd. H_2SO_4 and the resulting indigosulfonic acid dild. so that it is 0.05-0.01 N with respect to indigo and 0.2-0.5 N with respect to H_2SO_4 , passage through a Cd reductor will result in the formation of indigo white which can be titrated electrometrically with $FeCl_3$ soln. $C_{16}H_{14}N_2O_2 + 2 Fe^{+++} \longrightarrow 2 Fe^{++} + C_{16}H_{14}N_2O_2 + 2 H^+$. W. T. HALL.

The solubility of arsenic trichloride in concentrated hydrochloric acid at 100°. W. D. TREADWELL. *Helvetica chim. acta* 5, 818-21(1922).—In all of the numerous papers that have appeared upon the detn. of As by volatilizing $AsCl_3$, there is little mention of the least possible quantity of HCl required. Assuming that the law of Henry holds for the soly. of HCl, an integration formula is derived to show the relation between the vol. of the As soln. and the vol. of HCl gas required in the distn. process. This formula is tested experimentally and apparently holds true. In the detn. of As by the distn. method, the temp. should be at least 100°. Starting with 100 cc. of As soln., it is estd. that 19.8 l. of HCl gas are required to distil off 99% of the As as $AsCl_3$ and 20.7 l. of HCl to remove 99.9% of the As. At 100° the satd. soln. of $AsCl_3$ and HCl contains 100.3 g. of $AsCl_3$ per l. W. T. H.

Quantitative analysis by measuring the supersaturation tension of reactions. E. F. HOPPLE. *Chem.-Zig.* 46, 957-8(1922).—In extremely dil. solus. the time required for a visible ppt. to form is a measure of what may be called the *supersaturation tension*. This tension, like the speed of reactions in general, is dependent upon the temp. and concn. of the soln. At a const. temp., therefore, the concn. of a very dil. soln. can be estd. by observing the time required for a visible ppt. to form. If for a series of solns. contg. from 5 to 100 mg. of SO_4^{--} , Ca^{++} or NO_3^- per l., the time in secs. for a ppt. to appear at 15° is plotted against the concns., a parabolic curve is obtained in each case, which indicates the correctness of the assumption that these supersatd. tensions may be used for quant. estns. of constituents of natural waters. For SO_4^{--} detns., pptn. with Ba^{++} was studied, for Ca^{++} pptn. with $C_2O_4^{--}$ and for NO_3^- the formation of starch iodide with KI. W. T. H.

Electrometric titration of sulfurous acid with permanganate. W. S. HENDRIXSON AND L. M. VERBECK. *J. Ind. Eng. Chem.* 14, 1152-3(1922).—Treatment of an acid

soln. with an excess of KMnO_4 , adding KI and then KMnO_4 again until an end pt. was obtained electrometrically, indicated that H_2SO_4 is not completely oxidized to H_2SO_5 by KMnO_4 . A permanganate titration of H_2SO_4 appears to be impracticable, if not impossible.

W. T. H.

Quantitative determination of carbon and hydrogen by means of sulfochromic mixture. L. J. SIMON AND A. J. A. GUILLAUMIN. *Compt. rend.* 175, 525-7(1922).—Successful detns. of C and H were made with Ba formate, Na oxalate, oxalic acid, erythritol, saccharose, tartaric, benzoic and salicylic acids and phenolphthalein by a method which depends upon oxidation by means of a known wt. of $\text{K}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 soln., measuring the vol. of gas evolved and titrating the excess of dichromate with Fe^{++} and KMnO_4 .

W. T. H.

Rapid determination of ammonia in ammonium salts. H. BURKARDT. *Chem.-Ztg.* 46, 949(1922).—The formalin method for the detn. of NH_4 in salts has not received the attention it deserves. It is based upon the reaction, $6 \text{CH}_3\text{O} + 4\text{NH}_4^+ \rightarrow (\text{CH}_3)_4\text{N}_4 + 4\text{H}^+ + 6\text{H}_2\text{O}$. Dissolve $1/20$ of an equiv. of NH_4 salt in water, add about 20 cc. of CH_3O soln. and titrate with NaOH soln. using phenolphthalein as indicator.

W. T. HALL

Experiments on the oxide method of determining aluminium. J. E. CLENNELL. *J. Inst. Metals* (advance proof) 1922, 16 pp.—The described expts. were undertaken to ascertain the most suitable method for detg. Al in corrosion products such as are formed, for example, by oxidation of Al when Al amalgam is immersed under water. For the pptn. of dissolved Al, alkali nitrites, phenylhydrazine, KI and KIO_3 , and alkali thiosulfates were used and the last precipitant was found to be most satisfactory. The following method of pptn. is recommended: Of the HCl or H_2SO_4 soln. from which SiO_2 and metals of the Cu-Sn group have been removed in the usual way, take enough to correspond to about 0.1 g. of Al. Boil, if necessary, to expel H_2S , make slightly alk. with NH_4OH and dil. to about 300 cc. Into the slightly warm soln., introduce SO_2 until the ppt. dissolves and the soln. is colorless, or becomes so on standing. Add a few drops of methyl orange indicator and 3 N NH_4OH until the indicator becomes orange but no permanent ppt. is obtained. Add 5 g. $\text{Na}_2\text{S}_2\text{O}_4$, boil 30 mins., dil. to 500 cc. with 1% NH_4Cl soln., stir and allow to settle 10 mins. Decant through a filter, wash twice by decantation, using first 500 and then 300 cc. of 1% NH_4Cl soln. and finally transfer the ppt. to the filter and wash with hot water till free from chloride. Ignite and weigh as Al_2O_3 . Test the filtrate by adding a little more $\text{Na}_2\text{S}_2\text{O}_4$. If a white ppt. is obtained, add it to the contents of the crucible. If it is reddish, dissolve the ppt. in HCl and reppt. as before. If considerable Fe is present but not more Fe than Al, add 10-20 cc. of 25% AcOH with the $\text{Na}_2\text{S}_2\text{O}_4$ in the first pptn. If more Fe is present, and the first ppt. is yellow, dissolve it in HCl and ppt. a second time. Run a blank test on the reagents.

V. O. HOMERBERG

The determination of aluminium as phosphate. G. E. F. LUNDELL AND H. B. KNOWLES. *J. Ind. Eng. Chem.* 14, 1136-7(1922).—The values obtained when Al is detd. as AlPO_4 are not altogether satisfactory. In only 8 out of 22 expts. performed at the Bureau of Standards did the ppt. weigh within 2 mg. of the normal value. Fe^{+++} under the same conditions gave about the same results but, as might be expected, ppts. of $\text{Ti}_2(\text{PO}_4)_3$ invariably contained an excess of TiO_2 . The pptn. of AlPO_4 in the presence of Fe^{++} was not studied.

W. T. H.

Determine sulfur by the evolution method. E. V. HILLMAN. *Foundry* 50, 837-8 (1922).—Directions are given for carrying out this well known method in the analysis of steel and the chemistry involved is explained in detail.

W. T. H.

A rapid method of analysis for dolomite and magnesians limestone. S. D. AVERRITT. *J. Ind. Eng. Chem.* 14, 1139-40(1922).—A proximate analysis of minerals of this type may be made on the assumption that the % of CaCO_3 and MgCO_3 can be found by de-

ducting the % of moisture, % of insol. residue and % of $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ from 100% and that by detg. the vol. of HCl required to dissolve the sample enough data are obtained to est. the % CaCO_3 and of MgCO_3 . The method involves, therefore, only 3 detns.—that of moisture, that of insol. residue with ignited NH_4OH ppt., and titration of the excess acid used in dissolving the sample. W. T. H.

Colorimetric determination of phosphorus in minerals and in coke. MISSON. *Ann. chim. anal. chim. app.* 4, 267-9(1922).—The method depends upon a comparison of the color produced by the addition of $(\text{NH}_4)_2\text{MoO}_4$ to a soln. contg. H_3PO_4 and HVO_4 . For minerals contg. 0.01–0.2% P, prep. a set of 10 standards as follows: In each of 10 flasks place 1 g. of steel contg. 0.02% P and varying amts. of standard $(\text{NH}_4)_2\text{HPO}_4$ soln. (1 cc. = 0.1 mg. P) to make the standards as desired. Add 25 cc. of 6 N HNO_3 , after there is no more action in the cold, heat to boiling and add 10 cc. of KMnO_4 soln. (8 g. per liter). Boil 2 mins., remove the flame, add 10 cc. of H_2O_2 soln. (prepd. by adding slowly about 40 g. of Na_2O_2 to 1 l. of 10% HNO_3) and 10 cc. of HVO_4 soln. (prepd. by dissolving 2.345 g. of NH_4VO_3 in 500 cc. of hot water, adding 20 cc. of concd. HNO_3 and dilg. to 1 l.). Boil to destroy excess of peroxide, add 10 cc. of freshly prepd., 10% $(\text{NH}_4)_2\text{MoO}_4$, cool, dil. to 80 cc. and transfer to an Eggerts' comparison tube. Such standards keep about 1 week. In the analysis of the mineral, treat 1 g. of the powdered sample and 1 g. of steel with 10 cc. of 6 N HNO_3 and 30 cc. of 6 N HCl. After the decompn. of the ore, evap. to dryness, take up in 10 cc. of HCl, add 40 cc. of boiling water and filter. Evap. the filtrate to 5 cc., add 10 cc. HNO_3 and evap. again, repeating these operations twice more to make certain that all HCl is removed. Finally add 25 cc. of HNO_3 and treat with KMnO_4 , H_2O_2 , HVO_4 and $(\text{NH}_4)_2\text{MoO}_4$ as in the prepn. of the standards. Similar procedures are given in detail for the analysis of minerals contg. 0.2–2.5% P and for the detn. of P in coke. W. T. H.

A new method for the gravimetric determination of germanium. J. H. MÜLLER. *J. Am. Chem. Soc.* 44, 2493-8(1922).—To 100 cc. of soln. contg. Ge salt equiv. to 0.2–0.5 g. of GeO_2 , add 15–25 cc. of N MgSO_4 soln. (not MgCl_2 owing to volatility of GeCl_4 on ignition) and 25 cc. of 2 N $(\text{NH}_4)_2\text{SO}_4$ soln. Then add 15–20 cc. of concd. NH_4OH , stir and heat until the liquid has boiled a few moments. After 10–12 hrs., filter and wash with a limited vol. 1.5 N NH_4OH . Ignite in a porcelain crucible and weigh as Mg_2GeO_4 after strong ignition. This *magnesium orthogermanate* does not appear to have been described previously. Less than 0.5 mg. of Ge will pass into the filtrate when not over 50 cc. of wash water are used. The ppt. is amorphous and forms slowly in the presence of NH_4 salts. It contains, theoretically, 56.45% GeO_2 and analyses gave values ranging from 56.20 to 56.72% GeO_2 . This shows that the method will give fairly satisfactory results, probably as good as those obtained by the conventional and more laborious procedures. W. T. H.

Alumina as an absorbent for water in organic combustions. H. L. FISCHER, H. L. FAUST AND G. H. WALDEN. *J. Ind. Eng. Chem.* 14, 1138-9(1922).—By mixing about 24 g. of 12-mesh pumice with 100 cc. of 50% $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ soln. and heating in an elec. muffle until no more HCl was evolved at 700–750°, a mixt. of pumice and Al_2O_3 was obtained which is well suited for absorbing H_2O in the ultimate analysis of org. compds. From 50 g. of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ about 10.7 g. of Al_2O_3 is obtained which should be capable of absorbing about 1.92 g. of H_2O . W. T. H.

Neutralization of tartaric acid by potassium hydroxide in the presence of alkaline earth chlorides. L. J. SIMON AND L. ZIVY. *Compt. rend.* 175, 620-4(1922).—When tartaric acid is titrated with KOH, 1 mol. of base is used per mol. of tartaric acid if phenolphthalein is the indicator and 2 mols. with methyl orange. The presence of KCl makes the titration easier with phenolphthalein. If, on the other hand, an excess of CaCl_2 is added to the soln. the titration is the same with phenolphthalein as indicator

as with methyl orange: Ca tartrate is pptd. and 2 mols of KOH are required for each mol of tartaric acid.

W. T. H.

Reactions between gaseous oxides of nitrogen and alkali solutions (SANFOURCHE)
 6. Purifying sodium hyposulfite [with method of analysis] (CHRISTIANSEN, NORTON)
 18. Capillary flow, diffusion and displacement [washing precipitates] (LUMIÈRE) 2.
 Silver and halogen determination in photographic preparations (LEHMANN) 5. Method
 of the French Codex for the detection of iodates in potassium iodide (LACHATYRE) 17.
 The relation between volume and combining capacity (EPITRAIM) 2.

8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

Ninth list of new mineral names. L. J. SPENCER. *Mineralog. Mag.* 19, 334-54 (1922).—A list of 147 mineral names, arranged alphabetically, which have appeared in the recent literature. Many represent new mineral species. The name is followed by a brief description, including compn. of the mineral, and references. W. F. HUNT

Properties of the blue amphiboles. G. MURGOCI. *Compt. rend.* 175, 372-4 (1922).—The blue or violet shades and the intensity of the coloration of the blue amphiboles vary according to the no. of mols. of the type $\text{Si}_2\text{O}_5(\text{Al, Fe})$ (Na, K) and according to the ratio $p\text{Fe}_2\text{O}_3$ to $q\text{Al}_2\text{O}_3$. But these sesquioxides as well as the alkalis may exist in other states in the amphiboles, for types exist with sesquioxides deprived of alkalis or very low in alkalis which do not show the blue color. Also there are amphiboles rich in alkalis and with sesquioxides low or absent, which do not show a pleochroism of blue or violet. In any case blue and black amphiboles should be classed according to their content of MgO and the total proportion of the sesquioxides, and varieties be distinguished by the ratio $p:q$. The relation between these ratios and the optical properties is probably complex, but may be simple. The blue shade always appears to follow the crystallographic axis c , without regard to the orientation of the ellipsoid of optical elasticity. Characteristic shades of violet, grayish blue, olive green or reddish follow the axis b . In the direction of axis a are found clear colors of yellow, green or brownish to colorless. The relations of color to optical and crystallographic characters are further discussed in detail. Cf. following abstract. L. W. RIGGS

Classification of blue amphiboles and of certain hornblendes. G. MURGOCI. *Compt. rend.* 175, 426-9 (1922); cf. preceding abstr.—The minerals in the following lists are described mainly by their optical and crystallographic properties and the varying proportions of Fe_2O_3 to Al_2O_3 : Blue amphiboles: imerinite, torendrikite, glaucophane, gualadite, barroisite (carinthine), arfvedsonite, riebeckite, lanfite, hudsonite, speziatite. Certain hornblendes in which the classification appears to be based mainly on the ratios of MgO to FeO and Fe_2O_3 to Al_2O_3 are anophorite, barkevicite, bergamaskite, norallite, weinschenkite, linosite and kärsutite, carinthine, soréite, philipstadite, gamisgradite, and rimpylite.

L. W. RIGGS

Cyprine and associated minerals from the zinc mine at Franklin, N. J. J. V. LEWIS AND L. H. BAUER. *Am. J. Sci.* 4, 249-51 (1922).—"The following notes refer chiefly to cyprine, the sky-blue variety of vesuvianite, in intimate microscopic mixt. with willemite, and to the associated rhodonite (var. bustamite) and andradite (var. polyadelphite)." The cyprine showed properties in agreement with those published independently by Shannon (*C. A.* 16, 3453). Rhodonite var. *bustamite*. This agreed essentially with that recently described by Larsen and Shannon (*C. A.* 16, 3048). Andradite var. *polyadelphite*. Analysis by Bauer gave: SiO_2 34.28, Al_2O_3 3.12, Fe_2O_3 25.53, MnO 7.41, CaO 29.20, MgO 0.39, sum 99.93%. Besides minerals named above

phlogopite is also abundant in scales and crystals, and in places coarse cleavable feldspars occur. Pyrite, calcite and pyroxene are present in minute amounts. L. W. R.

Corundum in India. J. C. BROWN. *Bull. Indian Ind. Labour No.* 12, 1922.

O. P. R. OGILVIE

Glauconite from the green sand near Lewes, Sussex; the constitution of glauconite. A. F. HALLIMOND. *Chemical analysis.* E. G. RADLEY. *Mineralog. Mag.* 19, 330-3 (1922).—The grains, sepd. by sieving, had mean $n = 1.62$ and sp. gr. ≈ 2.70 . Analysis gave: SiO_2 48.12; Al_2O_3 9.16; Fe_2O_3 19.10; FeO 3.47; CaO 0.76; MgO 2.36; K_2O 7.08; Na_2O 0.22; H_2O (105°) 4.78; $\text{H}_2\text{O} > 105^\circ$ 5.28%. In order to det. the constitution of the mineral many analyses were recalcd. in mol. proportions. The proportion of alkalis was found to be quite const. and no evidence of the substitution of these by H_2O or by the magnesia group was detected. There is considerable replacement of the K_2O by Na_2O . In the groups R_2O_3 and RO the mol. proportions are not constant and indicate no relationship to the silica and alkalis. If the $(\text{Fe}, \text{Mg})\text{O}$ and $(\text{Fe}, \text{Al})_2\text{O}_3$ are considered as mutually replaceable, the ratios obtained lead to the formula, $\text{R}_2\text{O}_4(\text{R}_2\text{O}_3, \text{RO})$. $10 \text{ SiO}_2, n \text{ H}_2\text{O}$, the ratio of bases to silica being 1:2.

W. F. HUNT

The structure and composition of the Strathmore meteorite. W. E. P. McILIN-ROCK AND F. R. ENNOS. *Mineralog. Mag.* 19, 323-9 (1922).—Sections under the microscope show grains of Ni-Fe and troilite in a granular matrix of olivine and bronzite with a few chondrules of the same 2 minerals. In addition acid plagioclase was noted and sporadic patches of a clear, colorless phosphate mineral with low birefringence and high relief, which may be either apatite or merillite. Complete analyses are recorded of the attracted and unattracted portions as well as of the bulk material. From the bulk analysis the following mineral compn. was computed: feldspar 10.93, ilmenite 0.27, chromite 0.65, magnetite 0.51, apatite 0.56, olivine 41.13, bronzite 30.91, troilite 6.29, Ni-Fe 8.62, H_2O 0.17. Sp. gr. 3.53. The ratio of $\text{Fe}:\text{Ni}$ in Ni-Fe ≈ 5.80 ; $\text{MgO}:\text{FeO}$ in olivine 3.27; $\text{MgO}:\text{FeO}$ in pyroxene 4.25; $\text{MgO}:\text{FeO}$ in ferromagnesian silicates 3.47. The compn. of the olivine is expressed by the formula $3.27\text{Mg}_2\text{SiO}_4\text{Fe}_2\text{SiO}_4$. The Strathmore meteorite belongs to Group 3, Barotí type of Prior's classification (C. A. 14, 3622).

W. F. HUNT

Ore deposits of the Sierrita Mountains, Pima County, Arizona. F. L. RANSOME. U. S. Geol. Survey, *Bull.* 725-J, 21 (1922).—These mountains sep. the Papago district on the west from the Pima district on the east, the area surveyed being 20 to 30 miles southwest of Tucson. Over 40 claims and a dozen shafts in the Papago district are briefly described. Good ore has been found at many places but has come from small deposits and shallow workings which have been enriched by the chem. action of descending solns. and is not representative of what may be expected at depths of several hundred ft. In the Pima district a dozen productive mines are described. The yields of Cu, Pb, Zn, Au, and Ag from 1907 to 1919 show large annual fluctuations, the highest approx. figures being Cu 6 million lbs., Pb 1 million, Zn 2 million, Ag 100439 oz., and Au \$2283. A more intense mineralization is evident on the east side of the Sierrita Mountains than on the west side, particularly in Cu ores of the contact-metamorphic type. The outlook for finding additional sphaleritic Zn ores is good.

L. W. RIGGS

Mineral resources of Alaska. Report for 1920. A. H. BROOKS. U. S. Geol. Survey, *Bull.* 722, 7-67 (1922).—Though the mining industry of Alaska was depressed in 1920, yet the value of the total output was greater than in 1919 on account of the increase in the production of Cu. This paper gives the statistics of mineral production of the territory for the past 40 years, the new developments for 1920, and the general features of the mining of Au, Ag, Cu, Pb, Pt and other minerals of the Pt group, Hg, Sb, coal and petroleum. Water power investigations in southeastern Alaska are reported by Geo. H. Canfield, measurements having been taken from 25 stations, 18 of

which were in operation in 1921. **Ore deposits of the Salmon River district, Portland Canal region.** L. G. WESTGATE. *Ibid* 117-40.—Nearness to tide water and a comparatively mild climate are factors in favor of profitable mining in this region. No productive mine has yet been developed on the American part, and only one (Premier) on the Canadian part. The Ag deposits are primary sulfides and show no changes from weathering or downward enrichment. Six mining properties with 5 to 17 claims each are described. Sixteen tons of high grade Cu-Ph ore, and contg. small amts. of Au and Cu, have been shipped from one of the properties. **Gold lodes in the Upper Kuskokwim region.** C. C. MARTIN. *Ibid* 149-61.—These Au deposits were discovered in 1919-20 and are a decidedly encouraging feature of recent Alaskan mining. The Au is associated with granitic rocks, which are intruded into limestone and other little altered sedimentary rocks. Assays believed to be reliable give 2 or 3 oz. of Ag and \$55 to \$65 of Au per ton. "A large proportion of the ore assays \$30 to \$35 per ton for a full stoping width." Some of the ore contains 2% or more of Cu, and a little Ni was found in one sample. Eight shafts or excavations are described. **Metalliferous lodes in southern Seward Peninsula.** S. H. CATHCART. *Ibid* 163-261.—This paper outlines certain features of mineralization that were observed in an examn. of 110 prospects. Fe, Bi, W, Au, Cu, Ph, Zn, Sb and graphite have been found in bedrock and Hg is known in the placers. The sequence of mineralization may have been: (1) the older quartz veins which antedated the extreme metamorphism of the metamorphic series; (2) replacement deposits at limestone-schist contacts and along zones of bedding-shear in limestone; (3) the later quartz veins; and (4) sulfide mineralization. Pt is recovered from the placers of Dime creek incidentally to the mining of placer Au. On account of the difficulty in detg. Pt analytically the metal is frequently reported in ores when it is not present. Only specially qualified chemists are able to make trustworthy detns. of this element in ores. Lode Sn is known only in the York district. Au lode deposits are described in the Bluff, Solomon, Council and Iron Creek districts. Graphite deposits in the Kigluaik Mts. appear to be favorable for development. A composite sample of Fe ore from Monarch group of claims gave on analysis by R. C. Wells: SiO_2 5.53, Al_2O_3 1.34, Fe_2O_3 78.30, MgO 0.10, CaO 1.97, MnO 1.37, P_2O_5 0.13, CO_2 1.10, H_2O 10.40, sum 100.24%. L. W. RIGGS

The Skorovas iron pyrite deposit, Norway. H. H. SMITH. *Bull. Inst. Mining Met.* No. 217, 1-13(1922).—This deposit is situated at about 65° N. lat., 93.5 km. from the port of Namsos. Explorations show that it contains 2 to 3 million tons of high grade pyrite ore. 70% of the ore contains 47-51% S; 4 analyses are given. The ore is practically free of As and Se, and is low in Zn. This is a syngenetic deposit, associated with gabbro. E. F. H.

Nitrate deposits in the Amargosa region, southeastern California. Preface and introduction. H. S. GALE AND L. F. NOBLE. U. S. Geol. Survey, *Bull.* 724, 1-21 (1922).—The investigations by the Geol. Survey of the nitrate deposits in the U. S. were started in 1911 (cf. Gale, *C. A.* 6, 3388). The World War caused additional effort to be made so that by the end of 1918 nearly every reported nitrate deposit in southeastern Cal. had been investigated. The region studied lies principally in San Bernardino and Inyo counties. The nitrate deposits are associated with Tertiary clay beds which make the "mud hills" of this region. These hills have a bed-rock of upturned clay shale and sandstone upon which is a layer of "caliche" usually less than 6 in. thick and covered by a layer of soil usually less than 1 ft. thick. This soil for a depth of a few in. consists of a clay crust, underneath which is a loose powdery layer contg. much sol. material, chiefly Na_2SO_4 , CaSO_4 and MgSO_4 . Vegetation is practically absent. The most abundant salt in the caliche is NaCl. Sulfates of Na and Ca are usually present and NaNO_3 is present in much greater amts. than in the soil or bedrock. A review of previous work

on nitrate deposits is given and the plans of the present investigation are described. **South Death Valley region.** L. F. NOBLE AND F. C. CALKINS. *Ibid* 22-59.—In general the caliche of this area yielded less than 2% NaNO_3 . **Middle Amargosa Region.** G. R. MANSFIELD AND F. C. CALKINS. *Ibid* 59-89.—Very little of this area yielded caliche with more than 5% NaNO_3 . **General summary.** G. R. MANSFIELD. *Ibid* 89-93.—In the course of this exploration scores of trenches and hundreds of pits were dug from which samples were taken for quant. analysis. Thousands of brown ring tests were made, which were of special use in eliminating the less promising areas. Contrary to earlier optimistic reports the caliche in general is of poor quality, averaging less than 2.5% NaNO_3 and is very unevenly distributed. It is estd. that the most promising parts of the region, known as the Upper and Lower Canyon fields, would yield less than 2000 tons. The available quantity is so small compared with the needs of the country that this region cannot be considered of com. importance. L. W. RIGGS

Structure of the Medill-Denison area, Oklahoma and Texas. O. B. HOPKINS, S. POWERS AND H. M. ROBINSON. U. S. Geol. Survey, *Bull.* 436-A, 33 pp. (1922).—Scores of wells have been drilled in this area but the majority have been abandoned or yield salt water. A few yield gas and a smaller number oil. The most promising areas are the Trinity sand and the Preston anticline. Wells must be drilled with care not to penetrate the water-bearing sand, which lies immediately below the oil and gas sand. L. W. RIGGS

The behavior of inclusions in igneous magmas. N. L. BOWEN. *J. Geology* 30, (supplement to No. 6), 513-70 (1922).—For the direct soln. of large quantities of foreign inclusions, large amts. of heat are required and it is not believed that the magmas contain the necessary superheat (heat above its crystn. range). On the other hand magmas may incorporate foreign inclusions by the method of reactive soln. and pptn. Granitic magma satd. with hiotite cannot dissolve olivine, pyroxene, or amphibole, but can react with them to convert them into biotite. Basic magmas will react with inclusions belonging to a later stage of the reaction series (more acidic), whereby the inclusions become a part of the liquid by pptg. their heat-equivalent of the phases with which the magma is satd. (basic minerals). The addition of highly aluminous sediments to a basic magma should bring about the formation of anorthite and enstatite mols. The addn. of limestone to basaltic magma may give rise to a liquid that is capable of pptg. mellilite; and some alk. rocks may form by further differentiation. W. F. HUNT

The eclogites of Norway. PENTTI ESKOLA. *Videnskapsselskaps Skrifter I*, No. 8, 118 pp. (1921).—A contribution to facies-petrology, the study of the relations between the chem. and mineralogical compn. of rocks (*C. A.* 15, 2605). In order that such studies may be possible, analyses of rocks should always be accompanied by at least a qual. enumeration of the minerals present in the exact specimen analyzed. Sepn. of rock minerals for analysis is best accomplished by the use of Clerici's soln. (*C. A.* 1, 1371), $\text{Ti}(\text{CHO}_2)_2 + \text{Ti}_2(\text{C}_2\text{H}_3\text{O}_7)_2$, evapd. until almandite with sp. gr. 4 floats. When analyses of pure constituents are available the compn. of a rock can often be calcd. with results probably as accurate as obtained by direct analysis, because of the unrepresentative character of the sample of a coarse-grained rock. It has been proposed to designate the *comps. of garnets* by mol. % of simple constituent minerals, but this is incorrect since the bivalent elements vary independently of the trivalent ones. A new method is proposed in which the bivalent and trivalent elements are calcd. separately to 100 parts, resulting in a statement like $(\text{Fe}_{38}\text{Mn}_1\text{Mg}_{61})(\text{Al}_1\text{Fe}_3)_2$, the group $(\text{SiO}_2)_{100}$ being omitted as common to all. In series low in Fe", a garnet may be simply characterized by stating in this manner the bivalent elements. Using 8 of the most dependable garnet analyses collected by Ford (*C. A.* 9, 2364) together with 8 new ones, the relations between x and compn. can now be plotted with such certainty as to permit

estn. of the compn. from the n in any member of the series. The range available is from pyrope with $\text{Fe}_{16}\text{Mg}_{50}\text{Ca}_{14}$ and $n = 1.7412$ to almandite with $\text{Fe}_{68}\text{Mg}_1\text{Ca}_4$ and $n = 1.8132$; plotting the ns against mol. % $\text{MgO} + \text{CaO}$ and $\text{FeO} + \text{MnO}$ yields a curve deviating from a straight line somewhat toward a higher n in the middle. By tabulating the mol. % of CaO in garnets from individual rock types it is found that a considerable uniformity within each type exists. Detailed petrologic descriptions are given of eclogites and the rocks enclosing them from numerous localities in Norway. New analyses are given of a no. of the rocks and of sepd. minerals, the compns. of minerals being also inferred in many cases from their sp. grs. and ns . At least 8 structural types of eclogite can be sepd., the structure being a function of the phys. conditions during and in part after consolidation, and varying independently of the chem. compn. While heretofore eclogites have been regarded as solely of metamorphic origin, the evidence that many of them are igneous is conclusive. They have been formed by differentiation of the same magmas which have yielded the associated gneisses, labradorite rocks, olivine rocks, etc. Interesting secondary changes have been observed in eclogite minerals. Jadeite-bearing pyroxene has become unstable on release of pressure and replaced by an intimate intergrowth or symplectite of Na-free diopside and Ca-Na feldspar. Reaction between garnet and diopside has often produced kelyphite rims of hornblende. The eclogites enclosed in gneiss often show amphibolitized border zones, representing a change from the eclogite to the amphibolite facies of a rock of essentially the same chem. compn. Still further changes toward the green-schist facies also occur. A detailed study of olivine and garnet inclusions in labradorite rocks shows that the garnet does not contain so much Fe as that in amphibolites and gabbros; but as the difference is not due to chem. compn. it must be of phys. origin. As these garnets are like those of the eclogites in $\text{Fe} : \text{Mg}$ relations, the segregations in the labradorite rocks are to be considered as eclogites in process of formation. To confirm the data in the literature as to the high Fe of amphibolitic garnets, some new analyses were made. In most cases it was impracticable to sep. the mineral entirely free from inclusions of quartz and magnetite, but the impurities did not prevent the demonstration that the garnet in these rocks is indeed dominantly almandite. E. T. W.

Composition of varicolored marls. TIMÉDAUT. *Compt. rend.* 175, 447-9 (1922).—The marls of the Keuper beds in the east of the Paris basin are distinguished from those of other marl beds by their brilliant tints which vary within a small space. The dominant color is reddish brown varying to violet, green, pale greenish gray and pale gray. Analyses of 3 extreme types gave a range of SiO_2 52.10-61.16, Al_2O_3 18.40-20.32, FeO 7.13-15.27, MnO 0.07-0.25, MgO 3.01-6.44, CaO 0.0-0.61, K_2O 4.76-7.37, Na_2O 1.72-5.52. These marls appear to consist of carbonates, a silicate which is not clay, its compn. approaching celadonite or "bravaisite," and detrital constituents in which white mica is abundant, accompanied by quartz. L. W. RIGGS

A plea for geophysical and geochemical observatories. T. A. JAGGAR. *J. Wash. Acad. Sci.* 12, 343-53 (1922).—So far geological study has been qual. and piece-meal and frequently with economic objects. Geological like astronomical expeditions may furnish a few interesting unrelated facts but the lasting quant. work in astronomy is done in observatories. To place geology on a scientific basis, well equipped geological observatories should be endowed for measuring the movements of the earth, the chem. reactions occurring in volcanoes and other parts of the earth's crust, and the chem., phys. and hydraulic facts of sedimentation in river basins. The observatories suggested should be equipped with labs. and shops for the construction of app. to meet the requirements of new problems and should be run by a staff of physicists, chemists and engineers with an ambition to det. facts and their quant. measurements rather than their economic applications. L. W. RIGGS

Occurrence of sulfate-reduction in the deep layers of the earth. C. A. H. VON WOLZOGEN KÜHR. *Proc. Royal Acad. Amsterdam* 25, 188-98 (1922).—Samples were taken by means of sterile spatulas from the cores of the drillings of 9 wells along the Sprengelkanaal. From 5 to 10 g. of the soil sample were added to a sterile culture medium consisting of water 1000, Na lactate 5, asparagine 1, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 0.5, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.01 g. in 150 cc.; the bottles were then filled to the neck, stoppered and kept at 25°. After a period of 3 to 20 days sulfate-reduction was evident by the changed color of the specimen caused by the formation of FeS . Samples from the 9 wells at depths from 6 to 35 m. were thus tested. The conditions for sulfate-reduction by *Microspira desulfuricans* are (1) absence of O , (2) occurrence of org. compds., and (3) the presence of sulfate and the required mineral compds. Org. compds. are present in the deep layers even when not detected by the eye, their presence being shown by the reduction of permanganate. Anaerobic cultures yield a much larger total of bacteria than aerobic cultures. It appears that bacteria derived from aerobic or anaerobic cultivation belong for the greater part to the facultative anaerobes. Aerobes showed some resemblance in forming acid from glucose, Prussian blue from ferric ferricyanide, the formation of H_2S from broth (PhCO test), the splitting of esculin, the formation of catalase and most often in the inability to ferment glucose. Spores were not formed. Anaerobes form nitrites from nitrates to a marked degree, split inulin, and form invertase. Van der Steen's theory as to the part played by Mn in the oxidation of org. matter in the soil is not accepted, as the evidence warrants the conclusion that oxidation of org. matter can be effected by *Microspira desulfuricans* without the additional influence of Mn compds. L. W. RIGGS

Nickel and cobalt in the biosphere. W. I. VERNADSKII. *Compt. rend.* 175, 382-5 (1922).—Bertrand and Mokragatz (cf. C. A. 16, 3724) have shown that Ni and Co are const. constituents of the soil. V. states that Ni and Co are present in all organisms so far tested. These include many plants and a few animals. The elements isomorphous with Mg, comprising Fe, Zn, Cu, Mn, Co, Cd and perhaps In, in the complex albuminous pigments of plants and animals play an important role in physiologic processes. L. W. RIGGS

9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

The iron ore deposits of the world. ANON. *Wirtschaft u. Statistik* 2, 563 (1922).—Estimates are given for the largest Fe-producing countries. France now ranks third, her resources being exceeded only by those of Brazil and U. S. C. G. F.

The application of flotation to the antimonial gold ores of the Minchison range. H. R. ADAM. *J. Chem. Met. Soc. S. Africa* 23, 3-9 (1922).—It was hoped to float the stibnite and leave the gold mostly in the tailing. This, however, is not very successful. It is possible to get fairly good gold recovery, about 88% on a 20.5 dwts. per ton ore, by amalgamation followed by flotation. It is thought that such a system might be used profitably by small mines. R. S. DEAN

Iron ore smelting in California. R. C. GOSROW. *Chem. Met. Eng.* 27, 490-3 (1922).—An historical sketch of the first locations of Fe-ore in Cal.; first tapping of Fe from a blast furnace in 1881; and the more recent electrothermic smelting at Heroult. Only two plants have operated on a com. scale. Neither of these is now running. Other plants have exptd. with the direct reduction of ore with fuel oil. L. J.

Manufacture and treatment of high-speed steel. H. K. OGILVIE. *J. Iron Steel Inst.* (advance proof) 1922, 11 pp.—The manuf. of high-speed steel in the basic-lined elcp. furnace is discussed. A consideration of the proper heat-treatment of high-speed steel is given. Also in *Engineering* 114, 630-1 (1922). V. O. HOMERBERG

The constitution of basic slag. A. SCOTT AND D. N. MCARTHUR. *J. West Scotland Iron and Steel Inst.* 29, 79-102(1922).—The paper gives detailed results of microscopic study of basic open-hearth and basic Bessemer slag. Polished and etched sections were examd. by reflected light and thin sections by transmitted light. The work of prior investigators is carefully summarized. Chemical analyses of the slags and of prominent constituents and their mol. formulas are given. Two silicophosphates, spinelloid compds. and free basic oxides were found. The work was preliminary to a study of the suitability of the various basic slags for *fertilizers*. Basic open-hearth slag contg. fluorspar showed low soly. No definite conclusions as to the relation between compn. and utility were reached.

JAS. O. HANDY

Proposed pyritic smelting in a reverberatory furnace. E. C. KING. *Eng. Mining J. Press* 114, 633-4.—A reverberatory furnace is described in which the grade of mat obtained in the pyritic smelting is of a very uniform character. Air pipes introduced through the side walls, along the hridge wall of the furnace, and submerged in the bath not only furnish O for the desired reactions, but thoroughly agitate the bath so that the reactions can take place to best advantage and all the heat generated by the burning S will be distributed. A continuous slag and mat overflow maintains a const. level at all times in the furnace. The danger of the liquid mat in a reverberatory furnace is minimized by use of a basic material for the furnace bottom. Great fuel economy is anticipated when the furnace is put into actual operation.

E. F. PERKINS

Heat balances of blast furnace and steel plants. W. TRINKS. *Blast Furnace Steel Plant* 10, 451-6(1922).—Ideal heat balance charts are given for (1) an uneconomical steel plant, (2) an av. American plant, (3) an economical steam-operated plant, and (4) an ideally operated plant. Per lb. of finished steel produced plant (1) uses 2.25 lbs. of coal; plant (2), 1.5 lbs.; plant (3), 1.065 lbs.; plant (4), 0.89 lbs.

L. J.

Pyrophoric flue dust from iron blast furnaces. J. W. GILLES. *Stahl u. Eisen* 42, 884-9(1922).—The flue dust from dry gas purifying chambers is pyrophoric, probably because of the presence of MnO.

R. S. DEAN

British Siemens furnace practice. FRED CLEMENTS. *Rev. metal.* 19, 469-98 (1922).—A consideration of the detailed schedules of British Siemens furnace practice and of a suggested design for a furnace with a hearth capacity capable of producing 100 tons of ingots per heat. The balance of chem. operations in the furnace during a single heat, the heat balance as deduced from the chem. balance, and the detn. of the heat distribution throughout the system are given in detail. Complete data are given in many tables, curves, and drawings.

W. A. MUDGE

A study of valves for furnaces. HAAKON HELLAN. *Blast Furnace Steel Plant* 10, 473-7(1922); illus.—A description of shut-off, regulating, and reversing valves at present used in gas-fired open-hearth furnaces, the dependence of flue lay-out on the type of valve used, and a new type of reversing valve, rapid in action and sealed by either water or tar.

LOUIS JORDAN

Crystallography and the knowledge of metals. V. M. GOLDSCHMIDT. *Z. Metallkunde* 13, 449-55, 518-24(1921).—Three methods of detg. crystal form are discussed, geometrical crystallography, chemical studies (etching tests) and X-ray examn. The last method is giving much information; it is discussed in detail. Six tables show the symmetry and structure (face-centered, cube-centered etc.) of many of the common metals and alloys.

R. S. WILLIAMS

The graphical representation of ternary and quaternary alloy systems. W. HOMMEL. *Z. Metallkunde* 13, 456-65, 511-8, 565-9(1921).—H. shows by means of a large number of diagrams of ternary and quaternary alloy systems whose cooling curves and microstructures have been detd. that it is possible to represent any multicomponent system by the use of rectangular coordinates. The methods described obviate the neces-

sity of using the triangular coordinates commonly employed in the study of ternary diagrams and also make the space models unnecessary. Many photomicrographs are given and the structural appearance is adequately explained by reference to the corresponding rectangular diagram.

R. S. WILLIAMS

The recrystallization of metals. Zinc. G. MASING. *Z. Metallkunde* 13, 425-8 (1921).—Zn was hammered cold and then rolled into sheets about 1 mm. thick. The metal was not polished but was surface-etched with very dil. chromic acid. Specimens were heated for different lengths of time at different temps. and then microscopically examd. The results are shown in a series of photomicrographs. The first change is a recrystn. leading to the formation of small primary crystals. No appreciable change is then noted until a temp. between 130° and 190° is reached, the temp. depending on the kind of Zn used. At this temp. secondary crystn. commences and slow heating to an increasingly higher temp. or prolonged heating at this const. temp. produces large grains. Rapid heating increases the number of crystal centers and so decreases the size of the secondary grains produced. The size of the secondary grains is a function of temp., time and rate of heating.

R. S. WILLIAMS

The recrystallization diagram of technical aluminium. E. RASSOW AND L. VELDE. *Z. Metallkunde* 13, 557(1921).—Al cubes were compressed to different amts. and annealed at various temps. to det. the effects of these factors on recrystn. and grain growth. The relations between compression, temp., and grain size are shown in a table and in a perspective diagram.

R. S. WILLIAMS

Influence of the method of deformation on the recrystallization diagram of aluminium. E. RASSOW. *Z. Metallkunde* 13, 558(1921).—The expts. described in the preceding abstract were repeated with Al which had been cold-rolled instead of compressed. Tables and a diagram show that the method of deformation is without effect on the recrystn. within the limits of the expt.

R. S. W.

Segregation phenomena. O. BAUER AND H. ARNDT. *Z. Metallkunde* 13, 497-506, 559-64(1921).—Segregation is influenced by three factors (1) alloy type, whether eutectic, solid soln. or compd., (2) difference in d. of the components and (3) the rate of cooling. Many alloys were studied and the results are shown in a series of photomicrographs and by numerous tables. Segregation is more marked in eutectic alloys than in other types, especially if there is a marked difference in the densities of the component metals. Two types of segregation are considered (1) "ingot segregation" referring to marked concn. diffs. in various parts of the ingot and "intercrystalline segregation" indicating the usual cored structure of rapidly cooled solid solutions. In practically all alloys of the solid-soln. type, intercryst. segregation and ingot segregation are both induced by rapid cooling. By slow cooling ingot segregation is wholly prevented and intercryst. markedly reduced though not always eliminated. In a very few special cases neither type of segregation is produced by sudden cooling.

R. S. W.

Structure of eutectics. F. L. BRADY. *J. Inst. Metals* (advance proof) 1922, 45 pp.—The conditions under which the 2 phases sep. in the formation of the eutectic, especially in the case of binary eutectics between metals and metallic compds., were investigated. The forms of the eutectics were divided into classes according to certain phys. properties of the components. The division proposed shows the considerable connection that exists between the phys. properties, especially surface tension, and the structure. A great many photomicrographs are included.

V. O. HOMERBERG

X-ray examination of inner structure of strained metals. I. Copper wires. ONO AKIMASA. *Mem. Coll. Eng. Kyushu Imp. Univ.* 2, 241-60(1922).—The X-ray interference figures for Cu and steel wires under various conditions of strain and annealing are represented by 18 excellent plates. The photographs for Cu under strain show lines radiating from the center which become more pronounced the greater the strain.

By a consideration of the angles between these and also intensities, it is found that the trigonal axis of face-centered cubic Cu coincides with the longitudinal axis of the wire but otherwise has random orientation—in other words shows the structure characteristic of fibers. Annealing destroys the symmetrical radiating lines and causes the appearance of spots indicative of agglomerated larger crystals. These structure phenomena are discussed in terms of the physical properties of strained and annealed metals.

G. L. CLARK

Salt baths for heat treating. SAM TOUR. *Trans. Am. Soc. Steel Treating* 3, 245-51 (1922).—The ideal salt bath would give no pitting action, max. life of the pot, and would not require careful washing of the piece of steel after quenching. The advantages and disadvantages are given of (1) cyaniding, (NaCN, NaCl, and Na₂CO₃), (2) tempering (NaNO₂, KNO₃, and NaNO₃), and (3) hardening (binary or ternary mixt. of CaCl₂, NaCl, KCl, BaCl₂, Na₂SO₄, and Na₂CO₃) baths.

W. A. MUDGE

The influence of antimony on red brass. J. CZOCHRALSKI. *Z. Metallkunde* 13, 276-81 (1921).—Studies of the mechanical properties, tensile strength, ductility, etc., of red brass contg. varying amts. of Sb alone or of Sb and Pb together are described and illustrated with photomicrographs and tables. Up to 0.3% Sb no harmful effects are found, although an increase above this figure is distinctly harmful. Lead may be present up to 5% if the Sb is kept below 0.3% without a marked reduction in strength. An increase in the Sb content usually allowed by specification is, therefore, suggested.

R. S. WILLIAMS

The influence of bismuth on red brass. J. CZOCHRALSKI. *Z. Metallkunde* 14, 70-2 (1922).—Expts. like those previously described were carried out with brasses to which Bi was added in varying amts. up to 1.7%. No effect was noticed until the Bi content exceeded 0.3%. The results obtained were better than would be obtained in practice. An upper limit of 0.1% Bi is recommended. A small percentage of Bi aids materially in pouring in the production of clean castings.

R. S. W.

Effect of superheated steam on non-ferrous metals used in locomotives. HENRY FOWLER. *J. Inst. Metals* (advance proof) 1922, 4 pp.; *Engineering* 114, 374 (1922).—The alloys used in the chief parts that are subjected to the action of superheated steam in locomotives are discussed. It is shown that an alloy which may prove satisfactory when not subjected to friction may be wholly unsuitable when it has a moving part working over it.

V. O. HOMERBERG

Effects of overheating and repeated melting on aluminium. W. ROSENHAIN AND J. D. GROGAN. *J. Inst. Metals* (advance proof) 1922, 11 pp.; *Engineering* 114, 414-15. —If Al of high purity is heated in an atm. consisting almost entirely of air, no serious deterioration occurs even at a temp. as high as 1000°. Expts. were also performed which appeared to indicate clearly that even when the Al has been reduced to a form in which a very large surface is exposed to atm. oxidation, repeated re-melting does not appreciably affect the quality of the metal.

V. O. HOMERBERG

Experiments with soft iron. RICHARD BAUMANN. *Z. Ver. deut. Ing.* 66, 825-6 (1922).—Tensile and impact tests from -3° to 600° show that the specially prepd. soft Fe from Krupp is similar in quality and properties to ordinary ingot Fe; the white Fe gives higher elongation values above 200° than the ingot Fe. The impact values show a sharp decline from 18° to -3°, a rise from 18° to 200°, a minimum in the curve from 300° to 500°, and a sharp rise above this temp. Microscopic examn. showed that the metal is very uniform throughout. The compn. is C 0.06%, Si trace, Mn 0.13%, P 0.010, and S 0.026.

W. A. MUDGE

Cast iron and its chemical composition. O. SMALLY. *Engineering* 114, 277-80 (1922).—The addition to molten cast iron of Ce, U, Ca, V, Al, Mg and Zr as deoxidizers did not improve the properties of the iron. The correct pouring temp. for cast iron depends

upon its compn. and for general practice should be 10% higher than the temp. at which solidification begins. A difficult casting was made from cast irons having different chem. compns. Cast irons whose P (0.09%) and Si (1.20%) contents are low give castings having the smallest shrinkage cavities. Six-in. cubes cast in green sand molds from low-P and low-Si cast irons were free from pipe, whereas cubes cast from high-P and high-Si irons had large shrinkage cavities. The size of the pipe decreases as the solidification rate increases. The cracking of castings may be prevented by (1) releasing or removing restricting cores while the casting is at red heat, (2) retarding the rate of cooling during the blue brittle range to about 10° per hour, (3) accelerating the cooling of the heavier sections or retarding the cooling of the lighter sections if conditions prevent the selection of an iron having a high stretching capacity. The strength of cast iron decreases as the temp. increases up to 500° . Above 500° the strength increases up to a max. at 900° and then falls off rapidly as the temp. is further increased. F. P. FLAGG

The limits of solubility of carbon in ternary steels. I. The system chromium-iron-carbon. KARL DAEVES. *Z. anorg. allgem. Chem.* 118, 55-71(1922).—Melts were made in magnesia crucibles with Swedish wrought iron, electrolytic iron and ferro-chrome, contg. a max. of 18.5% Cr and 1.7% C. The structures on cooling were martensitic and specimens were annealed for a long time at 800° before microscopic examn. The soly. of C is as follows: 0.15% with 13.75% Cr, 0.30% with 10.00% Cr, 0.57% with 5% Cr, 0.75% with 3% Cr, and 1.28% with 1.00% Cr. W. A. M.

Experiments on the flow of steels at a low red heat, with a note on the scaling of heated steels. J. H. S. DICKENSON. *J. Iron. Steel Inst.* (advance proof) 1922, 38 pp.; *Engineering* 114, 826-9, 378-9.—D. has investigated the mech. properties of steels and alloys in the heated state. The steels examd. consisted of a 0.30 and a 0.45% C steel, a Ni-Cr steel, a high-Cr steel, a high-speed steel, and a cast Ni-Cr alloy. The scaling of these steels when heated is also considered. V. O. HOMERBERG

The mechanical properties of some chrome-vanadium steels. J. S. VANICK. *Trans. Am. Soc. Steel Treating* 3, 196-217(1922).—A study of the mechanical properties of Cr-V steels to det. their practical value in the design and construction of app. in *N-fixation equipment*. The tensile properties, hardness and microstructure as affected by different heat treatments were detd. for a given series of Cr-V steels. The series selected could be readily classified upon changes in the concn. of C, V, and Cr. (1) In the C series, contg. from 0.15 to 1.20% C, 1.0% Cr, and 0.18% V, in the annealed state, an improved tensile strength and a lowered ductility resulted with an increase in C content. With heat treated specimens a similar effect occurred up to 0.60% C. A rise in hardness accompanied the increase in strength. (2) The V series contg. 0.30-0.40% C, 1.0% Cr and from 0 to 0.65% V in the annealed state showed an improvement in toughness over the corresponding C-Cr series. The tensile strength was only slightly affected. Heat treatment developed an improvement in the tensile strength and hardness. The ductility fell off rapidly when the V content exceeded 0.30%. High reduction in area which is maintained over the entire group of V-steels revealed the toughness or inherent ductility of this type of steel. (3) The Cr series contg. 0.30-0.40% C, 0.18% V, and 0-14.5% Cr, in the annealed state showed the tensile strength and hardness to remain quite uniform for increases in Cr content up to 2%. In excess of 2% Cr increased the strength and hardness at the expense of ductility. Heat treatment intensifies the effects of Cr indicated in the annealed specimens. Microscopic examn. showed the relation between mechanical properties and the addition of varying proportions of C, Cr, and V. In the annealed specimens the well known effect of Cr and V to form carbides results in the combination of a portion of these elements with Fe_3C . The concn. of Cr and V into complex carbides causes a constriction and disruption of the pearlitic areas and in turn releases more ferrite and distributes the cementitic lamellae more

widely. The release of a portion of the ferrite and the coincident reinforcement of the matrix by the distributed cementitic lamellae accounts for the greater toughness.

W. A. MUDGE

Nitrogenization of iron and steel by sodium nitrate. L. E. BENSON. *J. Iron Steel Inst.* (advance proof) 1922, 6 pp.; *Engineering* 114, 412-13.—Specimens of armco Fe and a 0.4% C steel were found to become nitrogenized after being heated at a temp. of 500° in a salt-bath contg. NaNO_3 . The rate of penetration in the case of armco Fe was found to be comparatively rapid during the first few hrs., but after 15 to 20 hrs. the rate remained practically the same at 0.02 mm. per hr. The rate of penetration in several steels appeared to be slower than in pure Fe. Mn influences the rate of penetration more than does C. The penetration was only slight in the case of an acid Bessemer steel contg. 0.89% Mn. A piece of nitrogenized armco Fe showed no signs of nitride after heating for 90 min. at 700°.

V. O. HOMERBERG

Corrosion of iron and steel. SIR R. HADFIELD. *Proc. Royal Soc. (London)* 101A, 472-87(1922).—It is shown that a small Cu content, 0.16 to 0.25%, is beneficial, provided the condition is that of bare metal exposed to atm. corrosion, especially in a sulfurous atm. No recorded tests have yet shown that coated metal would be benefited by a Cu content. A Cu content in steel may actually be deleterious in cases where Fe or steel is subjected to either total or partial immersion in natural waters, or some sort of liquid phase.

V. O. HOMERBERG

Steel-reinforced aluminium cables. H. SCHENKEL. *Elektrotechn. Z.* 43, 1153-6 (1922).

C. G. F.

The legal aspect of electrolysis (in Great Britain). (Corrosion.) P. M. HEATH. *Electrician* 89, 321-2(1922).

C. G. F.

Chromium steels and their recent applications. LEON GUILLET. *Rev. metal.* 19, 499-504(1922).—Cr is a hardening agent in complex steels; it finds greatest industrial applications when used in conjunction with other alloying elements such as Ni, V, W and Mo. Some pure Cr steels are used: (1) tools and forgings (1-2% Cr); drawing (3-5% Cr); magnetic work (2-6% Cr and 1% C); and stainless steel (12-13% Cr). The effect of heat treatment is briefly reviewed. Typical mechanical and physical properties are given in curves and photomicrographs.

W. A. MUDGE

Binary lead alloys. J. GOEBEL. *Z. Metallkunde* 14, 357-66(1922).—A study of the effect of various hardening agents on Pb. Data are given for Sb, Mg, As, Zn, and Sn; Bi, Hg, Cd, Na, Ca, Sr, and Rb will be included in a later paper. The alloys were made by melting pure metals in porcelain crucibles under H or KCl-LiCl salt mixts. Brinell hardness (20-kg. load, 4-mm. ball for 20 sec.) and sp. gr. measurements were made, on all alloys cooled as follows: (A) chill cast, (B) slowly cooled in furnace at 1°/min., and (C) slowly cooled as in (B) after aging for 3 months. The sp. gr. of the alloys decreases in all cases in almost direct proportion to the alloying element. The rate of cooling or aging was practically without effect. With hardness values of 47 for electrolytic Fe and 27 for pure Zn as standards, for (A) 90% Sb gave 31.0, 13% Mg 29.2, 41.1% As 21.3, and 90% Sn 17.0; for (B) all values were lowered 10 to 20%; for (C) the values were increased over those of (B), but were lower than those of (A) except for the 35-70% Sb alloys where the increase was about 15% over (A). Complete physical data are given in curves and tables; no microscopic exams. were made.

W. A. MUDGE

The antimony-bismuth system. MAURICE COOK. *J. Inst. Metals* (advance proof) 1922, 16 pp.—Thermal results obtained showed the liquidus curve to be unbroken, and the solidus to be horizontal up to 60% Sb. The microstructures of slowly and quickly cooled alloys reveal an apparent duplex structure, which can be rendered homogeneous with sufficiently long annealing. These results lead to the conclusion

that Sb and Bi form an isomorphous series. A diagram for the system is given.

V. O. HOMERBERG

Copper-rich aluminium-copper alloys. DAVID STOCKDALE. *J. Inst. Metals* (advance proof) 1922, 14 pp.; *Engineering* 114, 396-8.—The results of the expts. are embodied in an equil. diagram extending from 0 to 20% Al. Two methods were used for fixing the points—the taking of cooling curves and the micro-exam. of quenched specimens. A discussion of the various solid solns. and photomicrographs are included.

V. O. HOMERBERG

Silumin, a new light alloy. J. CZOCHRALESI. *Z. Metallkunde* 13, 507-10 (1921).—The alloy of Al and Si referred to as Silumin is described though its method of production is not given. Macrographs and micrographs show the fine-grained structure of the "modified" alloy as compared with the ordinary alloy. Various tables and charts showing the physical and chemical properties of the metal and a summary of its possible uses are given.

R. S. WILLIAMS

Patent law in relation to alloys. TH. LACH. *Z. Metallkunde* 13, 545-56 (1921).—L. discusses the German patent law.

R. S. W.

Duralumin—a digest of information. H. C. KNEER. *Trans. Am. Soc. Steel Treating* 3, 13-42 (1922).

W. A. MUDGE

Duralumin—its properties and commercial possibilities. W. B. SROUT. *Trans. Am. Soc. Steel Treating* 3, 226-30 (1922).—A review of the applicability of Duralumin in the aviation industry.

W. A. MUDGE

A new type of automatic temperature regulator and its application to heat-treating furnaces (NEWCOMB) 1.

Treating ores. W. J. MELLERSH-JACKSON. *Brit.* 184,501, Feb. 10, 1921. Ores, particularly complex low-grade Ag and Au ores, are prep'd. for lixiviation by heating in a furnace and spraying over them while incandescent a soln. of a nitrate or nitrite, with or without the addition of a small amt. of an acid or salt, or bringing into contact with them an externally produced nitriferous gas. The process is preferably carried out in a mechanically operated furnace. Cf. 172,356.

Treating oxidized copper ores. H. L. SULMAN, T. J. TAPLIN, W. G. PERKINS and H. F. K. PICARD. *Brit.* 185,242, June 9, 1921. Ores contg. oxidized Cu compds., such as silicates, carbonates, and chlorides, e. g., chrysocola, malachite, azurite, and atacamite, are crushed, heated in a reducing gas for 15 min. to 1 hr. at 150-400°, so that the metal is produced without melting or alloying and without fritting the gang. The product is cooled, not necessarily in the reducing gas, and leached, e. g., in an app. of the "Pachuca" type, with an ammoniacal solvent in presence of air or O. Cu is recovered by distg. off the NH₃, the carbonate being produced by slow evapn. if (NH₄)₂CO₃ is employed as solvent, and the black oxide by use of steam or boiling. Both are readily converted into high-grade Cu. Any sulfide in the ore remains unaffected by the process and may be recovered by the usual means. The process may be modified by reoxidizing the Cu at a moderate temp. prior to the leaching operation.

Copper and other metallic sulfates. H. BARDY. *Brit.* 184,402, Oct. 10, 1921. The metallic constituents of ores, sludges, metalliferous residues, metallic wastes, alloys, etc., are dissolved by treatment with H₂SO₄ and an amt. of HNO₃ equiv. to the metal to be dissolved, the process being carried out either under pressure, or in presence of a catalyst, or under the influence of both pressure and a catalyst. Suitable catalysts are Pt and the salts of metals with various valencies, such as V, Os, Ce and Mn. The invention is described with reference to Cu compds., and in an example a quantity of cupriferous waste corresponding to a total Cu content of 1000 g. is treated with 3 l. of

H₂SO₄ of 15.4% strength, and then with 940 cc. of HNO₃ of 36° Bé. Finally, a further 7 l. of H₂SO₄ are added, this acid contg. a catalyst, *e. g.*, 5 mg. of OsO₃ or about 1% of MnSO₄. The dissolving vessel is covered with insulating material, and after 5-7 hrs. the Cu is nearly completely dissolved. In another example, the soln. is effected in a heat-insulated autoclave. To start the reaction, a pressure of about 1.5 atms. is produced by electrolysis, insol. anodes being used, after which a period of two hrs. suffices to complete the process. The soln. of CuSO₄ obtained is electrolyzed, insol. anodes being used, and the electrolysis may be performed directly in the dissolving vessel, thereby enabling the entire process to be carried out in one operation. Cf. *C. A.* 16, 3056.

Extracting metals. ELEKTRIZITÄTWERK LONZA. Brit. 185,745, Sept. 7, 1922. Si-Ca alloy used as a reducing agent in metallurgical processes is employed in the form of a pressed mass or briquet. The binder employed may be water-glass, lime, cement, or clay, and Fe filings or other substances may be added to increase the sp. gr., or Al or its alloys to increase the reducing action and facilitate the formation of slags; while by the further addition of oxides or other compds. such as Mn ore, a metal such as Mn may be added to a metal bath.

Extracting lead and silver. F. E. ELMORE and CHEMICAL & METALLURGICAL CORPORATION, LTD. Brit. 184,628, June 8, 1921. In the treatment of Pb-Zn ores and concentrates by the acid brine process described in 151,698 (*C. A.* 15, 665), the proportion of Ag which dissolves with the Pb is increased by removing the H₂S when the Pb is nearly all extd., and continuing the digestion with the same or fresh brine (which may be more strongly acid) for a short time. The ZnS residue may be further leached with one of the solvents mentioned in 151,698 to remove any remaining Ag. The removal of the H₂S may be effected by adding a quantity of SO₂, which may be that evolved in the first stages of the treatment. Cf. 127,641 (*C. A.* 13, 2332).

Art of separating metals. R. L. PECK and T. F. TORELL. Can. 224,819, Oct. 17, 1922. Cu is sepd. from Cu-Ni solns. by cementation upon an excess of Cu-Ni mat while an equiv. of Ni is taken into soln. without exhausting the cementing capacity of the mat. The partially exhausted mat and cement copper is roasted, part of the Cu is leached out and the residue is dissolved to produce the soln. first referred to.

Iron sponge from iron ore. A. SINDING-LARSEN. Can. 225,444, Oct. 31, 1922. The pulverized Fe ore is acted upon by a gaseous reducing agent in a heated closed chamber; the gases are drawn off, condensed and preheated by means of part of the heat given off by the used gases and then led back to the reaction chamber.

Reducing iron ores. A. STANSFIELD. Can. 224,899, Oct. 17, 1922. The powd. ore mixed with carbonaceous material is fed into a reducing chamber from which the gases of combustion are excluded and passed with agitation through zones of increasing temp. and against the flow of reducing gases in the chamber. The material is then withdrawn and cooled in a non-oxidizing atm. App. is also specified. Cf. *C. A.* 16, 1066.

Ferrotungsten; ferromolybdenum. J. M. SKELLY, J. MERSON and CONTINUOUS REACTION CO., LTD. Brit. 184,843, April 23, 1921. Fe-W and Fe-Mo are obtained by the exothermic reduction of ores or mixts. contg. oxides of Fe and of W and Mo without the use of Al. The reducing agent is Si, which may be in the form of Fe-Si, and an oxidizing agent such as NaNO₃ is added. The ores may be first purified and roasted. Cf. 123,102.

Ferro-molybdenum. W. L. TURNER. Brit. 184,912, June 1, 1921. C-free ferro-molybdenum is obtained by the exothermic reaction of a mixt. of molybdenite, Al, Fe₂O₃, and pyrolusite or other material contg. MnO. The resulting molten alloy which may contain 60% of Mo and 1.5% of Mn, may be refined by stirring with a basic flux such as a mixt. of lime and fluorspar.

Open-hearth furnaces. G. L. DANFORTH. Can. 225,474, Oct. 31, 1922. The gas and air passages of the furnace terminate in parts at either end of the melting chamber; the roof, floor and walls of the chamber incline inwardly adjacent the parts and the passages diverge therefrom.

Regenerator for a metallurgical furnace. W. L. HARDER. Can. 225,467, Oct. 31, 1922.

Furnaces; coating metals. CALORIZING CORPORATION OF AMERICA. Brit. 184,839, April 19, 1921. In furnace app., more particularly intended for calorizing metals, comprizing a rotary retort with a connection by which a non-oxidizing gas can be introduced into the retort, a joint is provided between the rotating and non-rotating portions of the gas connection, and the non-rotating portion is pivotally mounted so that the joint will be maintained gas-tight even if the retort should rotate eccentrically. The ends of the retort are closed by doors bolted into recesses in the end flanges which take the whole wt. of the retort. The metal to be treated is placed in the retort with powdered Al, the air in the retort is displaced by N, and the charge is heated to 800° for a period depending on the material and the size of the articles. The charge is then withdrawn and fired for 20 min. at 700–800°. Al(OH)₃, or NH₄Cl with Zn, graphite, or Al(OH)₃, may be mixed with the Al powder.

Iron and steel manufacture. USINES METALLURGIQUES DE LA BASSE-LOIRE SOC. ANON. Brit. 184,957, July 2, 1921. Addition to 163,693. In prep. basic steel as described in the principal patent, hard or semi-hard steels with a high C content and practically dephosphorized are prep. by treating gray Fe by a one-stage blowing process and dispensing with the usual recarburizing agents by regulating the quantities of pig iron introduced into the bath. Owing to the fluidity of the material during treatment, and the elimination of projections during the blow, the converter may be filled with the max. wt. of charge capable of being dealt with by the turning or lifting app.

Alloys. H. A. SKELLEY, A. B. SMITH and CONTINUOUS REACTION CO., LTD. Brit. 184,844, April 23, 1921. Fe alloys contg. Cr with or without other metals such as W, Mo, V, Ni, Mn, or Ti, and with or without C, *e. g.*, stainless steel, high-speed steel, or rustless Fe, are obtained by the exothermic reduction by means of Si or ferro-silicon or oxides of Fe which may be in the form of mill scale, magnetic oxide, etc., in the presence of an oxidizing agent such as Na or Ca chlorate or nitrate. The Cr, and the other metals where these are used, are introduced before, during, or after the reaction, and the C is introduced as a constituent of the Cr or ferro-chromium used. Cf. 123,104.

Alloys. MITSUBISHI ZOSSEN KABUSHIKI. Brit. 183,803, June 22, 1922. An alloy for turbine blades consists of Cu together with 5–7% of Al, 3–8% of Ni, and 1–3% of Fe, the Cu and Al together being 90–96%, the Ni and Fe 4–10%. The alloy is improved by heating at 800° for a few hrs., then at 500–700° for 1–3 hrs., and finally cooling in H₂O, air blast, or otherwise.

Alloys. W. MATHESIUS and H. MATHESIUS. Brit. 186,124, Aug. 24, 1922. In a process for obtaining an alloy contg. Pb and Sr, an alloy of Pb, Ca, and Na is first made by causing metallic Na to react on a layer of CaCl₂ on a molten Pb bath. The layer of chlorides is then removed and replaced by a layer of Sr and Ba chlorides, whereupon Sr and Ba replace some of the Ca and Na in the alloy. A Pb alloy contg. 2% of Ca and 1% each of Sr and Ba may be so prep.

Iron alloys. ELEKTIZITÄTSWERK LONZA. Brit. 185,745, Sept. 6, 1922. Elements such as Si, Cr, or W to be added to a molten Fe bath are employed in the form of oxides or ores in admixt. with a reducing metal or compd. such as Al, Ca, Si-Ca, Si-Al, or the like. The mixt. may be briquetted with the aid of a binder.

Refining metals and alloys. GENERAL ELECTRIC CO. Brit. 183,217, April 15, 1921. Metals or alloys, particularly Si steel for use as magnetic material, are refined

by electromagnetically expelling slag particles from the molten metal and thereafter mechanically sepg. the refined molten metal from the supernatant layer of slag. The molten metal is subjected, subsequently to any chem. purification, to the action of a periodically varying magnetic field adapted to cause the slag particles to rise to the surface. A suitable construction is specified.

Alloys; casting metals. CALORIZING CORPORATION OF AMERICA. Brit. 184,840, April 19, 1921. Castings resistant to oxidation at high temps. are made from an Fe alloy contg. 19.5% of Al, the grain being refined by the addn. of 1-5% of Ni, Cr, V, Mn, Mo, W, Co, Zr, Si, U, B, Mg, Cu, or Ce to the molten mixt. of Fe and Al. To prevent oxidation during casting, the ladle and mold are filled with CO, and a blast of CO is directed on to the metal during its transference from the furnace to the ladle and from the ladle to the mold. The opening in the bottom of the ladle may be closed by a destructible diaphragm such as of thin metal or cardboard.

Coating metals. E. MERCK (Firm of). Brit. 185,082, Dec. 20, 1921. Objects of cerite metals or alloys are coated with other metals, in particular Al, Mg and Zn, by treatment while under continuous movement in closed vessels at temps. below the m. p. with the coating metals or mixts. in crushed, preferably powder, form with or without other materials such as C or sand. Al coatings may be obtained below 200°. Preliminary cleaning of the surface to be coated is unnecessary.

Tungsten carbides. AMT.-GES. B. FELDER-CLEMENT. Brit. 185,313, Aug. 15, 1921. In the production of tools or implements from W carbides (WC or W₂C), for instance by the process described in 157,747 and 157,750, it is desirable to heat to a temp. above the m. p. in order to vaporize impurities such as Fe, extra C is liable to be taken up, which seps. as free C on solidification. This free C is removed by adding a quantity of Mo, as carbide, metal, or oxide. The C is volatilized with the Mo or oxidized by the O of the Mo oxide without leaving any residual Mo. The carbide can thus be heated much above the m. p. so as to obtain a completely liquid mass from which sharp castings can be obtained, for instance by the process described in 157,750.

Casting-machines. L. CAMMEN. Brit. 184,472, Aug. 8, 1922. The mold of a centrifugal casting-machine is heated electrically, or by placing it in a furnace or by other means independent of the heat of the metal to be cast, to a temp. not less than 1/4 that of the m. p. of the metal to be cast. Special reference is made to metals which chill rapidly from the molten state, such as Monel metal or high-Cr steel.

Arc welding. INTERNATIONAL WELDING ENGINEERING CORPORATION. Brit. 183,876, Feb. 2, 1921. An electrode for use in elec. arc welding, formed of steel, Mg, W, etc., has a thin coating of the kind described in 144,333 (as distinct from a coating of inappreciable thickness of the kind described in 122,606) of Na or K silicate and BaCO₃. The coating is put on by smearing or dipping the electrode, and coloring matter may be mixed with the coating.

Solder paste. J. MAURER. Brit. 183,188, March 18, 1921. A solder-paste for uniting precious and other metals consists of finely divided metals corresponding to the parts to be joined, oxides thereof, a reducing agent, a binding medium, and a flux. The binding medium may consist of vaseline to assist the reducing agent, such as C. The flux may consist of borax or boric acid. For soldering 20-22-carat gold, the paste may consist of flux 4 parts, C 0.3, Au 833 fine 0.5, Au oxide 0.83, Ag oxide 0.12, and Cu oxide 0.05, together with 2-8% of vaseline. For 18-carat gold, the gold used is 750 fine, the proportions of Au oxide, Ag oxide, and Cu oxide are, resp. 0.75, 0.18, and 0.07 parts, and the same proportions of other constituents as for 20-carat gold. The solder may also contain Zn, Cd, etc.

Fluxes. I. A. INMAN and A. S. HARRIS. Can. 225,547, Nov. 7, 1922. A soldering flux contains glycerol 2, NH₄Cl 1 and ZnSO₄ 1 part.

10—ORGANIC CHEMISTRY

CHARLES A. ROUVILLER

Formation of lutadiene from ethylene. J. E. ZANETTI, J. R. SUYDAM, JR. AND M. OPPNER. *J. Am. Chem. Soc.* **44**, 2036-41 (1922).— C_2H_4 was passed through a tube heated to the desired temp. at such a rate (0.1-0.15 l. per min.) that it was in the hot section of the tube about 0.8 min.; the gas issuing from the furnace was passed through Br water and the unchanged C_2H_4 and the lutadiene (A) formed sepd. as $(CH_2Br)_2$ and $(CHBrCH_2Br)_2$, resp. A begins to form at 600° , reaches a max. (about 1% of the C_2H_4 supplied) at 750° and drops to 0% between 850 - 900° . The diminution in the amt. of A, beginning at 750° , is coincident with the beginning of the formation of aromatic compds. and it is suggested that the formation of the latter from C_2H_4 takes place, in part, at least, through the intermediate formation of A. The present is an example of the formation of an aliphatic hydrocarbon of higher h. p. from one of a lower b. p. and attention is called to the possible role of similar reactions in the cracking of oils.

C. A. R.

Oxidation of isopropyl alcohol with potassium permanganate. WM. L. EVANS AND L. B. SEFTON. *J. Am. Chem. Soc.* **44**, 2271-6 (1922); cf. *C. A.* **13**, 2368.— Me_3CHOH is oxidized by alk. $KMnO_4$ to CO_2 , $(CO_2H)_2$ and $AcOH$ at 25° , 50° and 75° ; in mixts. of low alkyl. Me_2CO is also formed in measurable amts. at 25° and in traces at 50° ; in media with an alkyl. of more than 2.12 g. KOH per l. no Me_2CO is formed. The production of $(CO_2H)_2$ and $AcOH$ increases and decreases, resp., as the initial alkyl. increases from neutrality to approx. 0.1-0.2 N concn. The general effect of temp. is to increase the yield of CO_2 in excess of 1 atom equiv. of C (see following abstr.). $(CO_2H)_2$ is obtained in greater amt. from Me_3CHOH than from Me_2CO in neutral solns. because in the first step of the reaction (Me_2CO formation) no acids are formed to neutralize the KOH obtained from the $KMnO_4$; furthermore, the course of the oxidation is such as to bring about a greater final concn. of alkali than in the oxidation of Me_2CO alone, and hence vinyl alc. formation takes place more readily.

C. A. R.

Oxidation of acetone with potassium permanganate. WM. L. EVANS AND L. B. SEFTON. *J. Am. Chem. Soc.* **44**, 2276-83 (1922); cf. preceding abstr.—Oxidation of Me_2CO with neutral or alk. $KMnO_4$ at 25° , 50° and 75° gives $(CO_2H)_2$, $AcOH$ and CO_2 . The yield of $(CO_2H)_2$ increases both with increase in temp. and with increase in the concn. of the alkali, while that of $AcOH$ diminishes with decrease in temp. and increase in the concn. of the alkali. The production of CO_2 increases with the temp.; in neutral soln. the Me_2CO should be completely oxidized to CO_2 at about 184° . The $AcOH$ and CO_2 are produced by the oxidation of AcH and $CH_3=$, resp. The presence of $(CO_2H)_2$ in neutral solns. is due to the very slow oxidation of $AcOH$ and the oxidation of vinyl alc. Me_2CO in H_2O must exist in equil. with $CH_3 : C(OH)Me$; increase in the concn. of the alkali increases the $CH_3 : C(OH)Me$ formation. The expts. of E. and S. confirm the views of Denis and of Witzemann that acetol is an intermediate product in the oxidation of Me_2CO ; the max. and min. effect observed for $AcOH$ and $(CO_2H)_2$, resp., at higher concns. of alkali in the oxidation of acetol were not noted in the present work.

C. A. R.

Tetranitromethane. V. Tetranitromethane as a nitrating agent. II. ERICH SCHMIDT, RICHARD SCHUMACHER, WILLY BÄJEN AND ARALBERT WAGNER. *Ber.* **55B**, 1751-9 (1922); cf. *C. A.* **15**, 3614.—By means of tetranitromethane (A) in the presence of C_6H_5N the H on C atoms carrying an olefin double bond can be replaced in certain cases by the NO_2 group but the position of the double bond with reference to an aromatic nucleus is a detg. factor; allyl aromatic derivs. are unchanged by A in C_6H_5N and Me_2CO while the isomeric propenyl derivs. are converted into the corresponding β - NO_2 compds. If

the reaction is carried out in alics. instead of C_6H_5N , not only is the NO_2 compd. formed but the double bond is destroyed by the addn. of the alic.: $-CH:CH- + ROH + (O_2N)_2C.O.NO_2 = -CH(OR)CH(NO_2)- + CH(NO_2)_2$. The conversion of some

tert. aliphatic-aromatic amines into sec. nitrosamines by means of A in the presence of AcOH is also described. From 7.4 g. *o*-anethole, 4.8 g. C_6H_5N and 9.8 g. A in Me_2CO with 6.7 cc. of 33% KOH in 50 cc. H_2O is obtained 3 g. β -nitro-*o*-anethole, $b_{D,4}$ 127-8°, crystals from petr. ether, m. 52-3°. β -Nitroisoeugenol methyl ether (4.2 g. from 4.5 g. $3,4-(MeO)_2C_6H_3CH:CHMe$), crystals from MeOH, m. 72°. β -Nitroasarone (3.7 g. from 4.2 g. asarone), yellow prisms from alc., m. 98-9°. β -Nitroisomyristicin (2.8 g. from 3.2 g. isomyristicin), m. 111-2°. β -Nitroisopipole (1.2 g. from 2.2 g. isopipole), yellow needles from alc., m. 110-1°. The following compds. were prepd. by slowly dropping 1 mol. A in alc. into 1 mol. of the unsatd. compd. in boiling alc., refluxing some hrs., adding H_2O and satd. NaCl, extg. with Et_2O , boiling the Et_2O ext. 20-30 min. with charcoal, filtering, shaking 3-4 hrs. with an aq. suspension of MgO , drying the Et_2O layer with Na_2SO_4 and distg. *in vacuo*. α -Methoxy- β -nitrodihydro-*p*-anethole (6.5 g. from 7.4 g. *p*-anethole), $b_{D,4}$ 133-5°, m. 49-50°, gives with Br (Meisenheimer and Jochelson, *C. A.* 2, 78) 60% of $p-MeOC_6H_4CH(OMe)CBr(NO_2)Me$. α -Methoxy- β -nitro-*o*-anethole (6 g. from 7.4 g. *o*-anethole), $b_{D,4}$ 127-8°, needles from C_6H_6 -petr. ether, m. 63-4°. α -Ethoxy- β -nitrodihydro-*p*-anethole (8.7 g. from 7.4 g. *p*-anethole), light yellow oil, $b_{D,4}$ 137°. *o*-Isomer (8.5 g. from 7.4 *o*-anethole), light yellow oil, $b_{D,4}$ 125°. α -Methoxy- β -nitrodihydroisosafrrole (7.4 g. from 8.1 g. isosafrrole), $b_{D,4}$ 138-40°, m. 67-8°. $p-O_2NC_6H_4N(NO)Me$, m. 100-1°, is obtained in 5 g. yield from 5 g. $PhNMe_2$ and 6.6 g. A in 3.6 g. AcOH and 20 cc. alc. heated 3 hrs. at 100° in a sealed tube. Similarly, $p-NCC_6H_4N(NO)Me$, m. 125°, is obtained in 87.1% yield from $NCC_6H_4NMe_2$ and 2.4 (O_2N) $_2C_6H_4NHf$, m. 113-4°, in 56.0% yield from (O_2N) $_2C_6H_4NEt_2$. C. A. R.

Decomposition of amines in the vapor stage. F. W. UFSON AND LILA SANDS. *J. Am. Chem. Soc.* 44, 2306-10 (1922).— $EtNH_2$ passed over kaolin at 500° gives chiefly NH_3 , HCN, C_2H_4 , a substance which is probably MeCN and small amts. of H and N; at 700° it gives more C_2H_4 and no HCN; at 1000° the chief products are the elements, although traces of C_2H_4 and probably of MeCN were found. $PrNH_2$ at 700° gives chiefly $EtCN$, NH_3 , C and hydrocarbons, with small amts. of HCN and the elements. Butane is formed from $EtNH_2$ at 1000°, and C_2H_4 and C_3H_4 as well as propane and propylene, from $PrNH_2$, results which can be accounted for only on the basis of the theory of methylene dissociation. C. A. R.

The oxidation of hydrocarbons, with special reference to the production of formaldehyde. B. W. BLAIR AND T. SHERLOCK WHEELER. *J. Soc. Chem. Ind.* 41, 303-107 (1922).—With an app. similar to that of Willstätter and Bommer (*C. A.* 15, 1295), in which mixts. of C_2H_4 and O are passed once at 405-540° through a heated tube contg. a Pt or Fe_2O_3 catalyst, no CH_2O was formed even when the rate of gas passage was very rapid. Without catalysts in the same app. heating for a shorter time at a higher temp. increased the yield, although the total conversion was decreased. In a new app. in which the gas mixt. was circulated through the reaction tube for as long as 24 hrs., yields of CH_2O as high as 70% were obtained. The use of steam in the gas mixt. tended to stabilize the CH_2O and prevent its immediate oxidation; NH_3 has a stronger stabilizing effect. The following scheme is believed to represent the course of the oxidation: $C_2H_4 \rightarrow CH_2:CHOH \rightarrow AcH \rightarrow CH_3(OH)CHO \rightarrow CH_2O \rightarrow HCO_2H \rightarrow CO_2 + H_2O$. The app. and many of the expts. are described in detail.

T. S. CARSWELL

The action of ozone on hydrocarbons with special reference to the production of formaldehyde. I. The action of ozone on methane. T. S. WHEELER AND E. W.

passed, and a trace of NH_4CN can be detected. When the Ni catalyst is replaced by platinized asbestos no reaction takes place; undoubtedly the nature of the catalyst must be such that an unstable carbonyl can be formed. C. A. R.

The conversion of sodium formate to oxalate. C. MATIGNON and (MILLER) G. MARCHAL. *Bull. soc. chim.* 31, 789-96(1922).—A series of expts. on the yield of $(\text{CO}_2\text{Na})_2$ formed by heating HCO_2Na under varying conditions indicates: 1st, that the decompn. of HCO_2Na occurs within 5 min. at 440° ; 2nd, that heating in air in the presence of a catalyst is as advantageous as heating *in vacuo* without a catalyst; 3rd that the introduction of 2% of NaOH or KOH as catalyst yields approx. 83% of $(\text{NaO}_2\text{C})_2$ as compared with a 53% yield in their absence. I. P. ROLF

Catalysis of the formation and hydrolysis of acetamide by acetic acid. W. A. NOYES and W. F. GORBEL. *J. Am. Chem. Soc.* 44, 2286-95(1922).—AcOH catalyzes both the formation of AcNH_2 from AcONH_4 and the hydrolysis of AcNH_2 by H_2O ; the latter reaction is autocatalytic, doubtless because the AcOH from the dissociation of the AcONH_4 formed catalyzes the reaction. The formation of AcNH_2 from AcONH_4 with or without the addn. of 0.1 mol. AcOH is essentially a dimol. reaction between NH_3 and AcOH, probably with the formation of an intermediate compd. $\text{MeC}(\text{OH})_2\text{NH}_2$ as an ephemeral step in the process. The formation and hydrolysis of AcNH_2 in the presence of 1.5 mols. AcOH is chiefly a dimol. reaction with 1 of the constituents, H ion or AcOH, const. The other constituent limiting the speed of the reaction must be NH_3 on 1 side and AcNH_2 on the other. By heating an equimol. mixt. of AcONH_4 and AcOH just short of boiling for 30-50 min. and then slowly distg. off the H_2O formed and the excess of AcOH, a 95-8% yield of AcNH_2 can be obtained. The velocity expts. were carried out by heating about 1 g. AcONH_4 or 0.75-0.8 g. AcNH_2 and 1 mol. of the other substance in a sealed tube in boiling xylene or anisole and detg. the AcONH_4 and AcNH_2 after the heating by Folin's method. The equil. point in the hydrolysis of AcNH_2 was detd. by approaching it from both sides; at 137° it lies at 77.05% AcNH_2 starting from AcONH_4 alone, 78.55% from AcONH_4 + 0.1 mol. AcOH and 75.50% from AcONH_4 + 1.5 mols. AcOH; at 152.5° , 79.99% from AcONH_4 alone. The speed of formation of AcNH_2 is about 3 times as great at 152.5° as at 137° . Addn. of 0.1 mol. NaOAc, 0.01 or 0.5 mol. NH_3 , 0.22 mol. NH_4HCO_3 or 0.03 mol. NaOH produces only small effects; 0.1 mol. HCl hydrolyzes somewhat more than an equiv. amt. of AcNH_2 in 30 min. and further hydrolysis proceeds at about the same rate as in the presence of 0.1 mol. AcOH. C. A. R.

The action of the glow discharge upon free fatty acids and their glycerides. EGON EICHWALD. *Z. angew. Chem.* 35, 505-6(1922).—When pure oleic acid is treated with the glow discharge in atm. of N, H, or air, the d no. drops and the mol. wt. rises. This was at first attributed to the combination of the unsatd. groups with each other, resulting in the formation of tetramethylene derivs. However, as the I no. dropped a corresponding amt. of stearic acid was formed, until a content of 14-5% was reached. On the basis of this discovery it appears that the action of the discharge upon oleic acid may be explained by assuming that H is split off from the acid mol. by the electronic bombardment, leaving highly unsatd. acids. This H then combines with a fresh mol. of oleic acid to form stearic acid, while the highly unsatd. acids polymerize to compds. of high mol. wt. This theory is borne out by the fact that after a time the stearic acid content reaches a max., and can only be increased by the addn. of fresh oleic acid. T. S. CARSWELL

Brassicidic acid anhydride and the preparation of anhydrides by means of phosgene. D. HOLDE and K. SCHMIDT. *Z. angew. Chem.* 35, 502-3(1922).—Pure erucic anhydride was prepd. by the method of Holde and Wilke (*C. A.* 16, 1564) and rearranged by means of HNO_3 to the isomeric *brassicidic acid anhydride* (A), m. 64° , d_4^{20} 0.835, difficultly

sol. in alc., crystg. from alc. in needles, from petr. ether and Et_2O in rhombic plates. *Brassicidic acid* with an I no. of 74.8 was prepd. by the rearrangement of erucic acid with HNO_3 ; in the same manner the Et ester of erucic acid gave the *ethyl ester* of brassicidic acid, m. 30–30.5°, n_D^{20} 1.4587, crystg. in 6-sided leaves. The anhydrides of the fatty acids in train oil were prepd. by the action of COCl_2 upon suspensions of their alkali salts in C_2H_5 , according to the method of Hentschel (*Ber.* 17, 1285(1884)), Hofmann and Shoetersack (*Ber.* 17, 623(1884)) and Hofmann (*Z. angew. Chem.* 21, 1986(1908)). The anhydride was a salve-like product of higher m. p. than the corresponding glycerides or the free acids.

T. S. CARSWELL

The constitution of soap solutions. Hexadecanesulfonic (cetylsulfonic) acid and other sulfonates. M. H. NORRIS, D. H. FALKNER AND M. C. PRICE. *J. Chem. Soc.* 121, 2161–8(1922).—Hexadecanesulfonic acid was prepd. by oxidizing the mercaptan with KMnO_4 . The Pb salt was decompd. with H_2S , giving a product resembling soft soap, which turns brownish black when the alc. is driven off by heat. The 0.75 *N* acid in alc. is a white or pale yellow sticky paste at room temp. and often has a shimmering appearance due to the presence of microcrystals. 0.1 *N*–0.02 *N* solns. have the consistence of boiled starch solns. and more dil. solns. are limpid and milky. The acid is a H soap having the typical behavior of a colloidal electrolyte in its cond., osmotic activity and high temp. coeff. of soly. Its place is among the highest soaps, between Na stearate and behenate. The behavior of α - and β - $\text{C}_{16}\text{H}_{33}\text{SO}_3\text{Na}$, and of $\text{C}_{14}\text{H}_{29}\text{SO}_3\text{Na}$ lends support to the assumption that the length of the mol. is an important factor in producing a colloidal electrolyte. Thus the α -form is less colloidal than the β -form and the ring compds. are far less colloidal than the open-chain compds. with the same no. of C atoms. The approx. solubilities of these salts are: α - $\text{C}_{16}\text{H}_{33}\text{SO}_3\text{Na}$, 82 g. per 100 cc. at 85°; β - $\text{C}_{16}\text{H}_{33}\text{SO}_3\text{Na}$, 32 g.; $\text{C}_{16}\text{H}_{33}\text{SO}_3\text{Na}$, 27 g.; $\text{C}_{14}\text{H}_{29}\text{SO}_3\text{Na}$, 3 g.

C. J. WEST

Monothioethylene glycol. GEO. M. BENNETT. *J. Chem. Soc.* 121, 2139–46 (1922); cf. C. A. 16, 409.—*Monothioethylene glycol* (A), b_{11} 55°, b_{14} 157–8° (slight decompn.), d_4^{20} 1.1317, d_4^{10} 1.1230, d_4^{20} 1.1143; n_D 1.4963, n_D 1.4996, n_F 1.5079; n_D 1.5151 at 20°; the viscosity at 20° was found to be 0.0322 C. G. S. units. It is completely miscible with Et_2O , C_2H_5 or H_2O . Mixture with an equal wt. of H_2O shows a contraction of 1% in vol. The following metallic salts were prepd. *Mercury compound*, $\text{Hg}(\text{SC}_2\text{H}_4\text{OH})_2$, large silvery plates, m. 123°. *Mercurichloride*, $\text{HOCH}_2\text{CH}_2\text{SHgCl}$, solid, m. 135–40°. *Lead*, orange plates, m. 110°. *Cuprous*, $\text{CuSC}_2\text{H}_4\text{OH}$, colorless but discolored by light, decompd. upon heating. A soln. of this salt, treated with A, gave the yellow *cupric compound*. *Silver*, sparingly sol. in cold H_2O . *Aurous*, pale yellowish gray solid. *Platinous*, pale, greenish gray solid. With excess of PtCl_4 , a yellow ppt. of the *platinic compound* was formed. *Cadmium*, m. 139° (decompn.). *Nickel*, dark brown needles. *Bismuth*, lemon-yellow needles, m. 79°. *Antimony*, m. 131°, sparingly sol. in all solvents except A itself. *Calcium*, by adding dry Et_2O to A in which Ca has been dissolved at 100°. *Monosodium*, cryst. deliquescent solid, by action of Na on A in dry Et_2O or PhMe. *Disodium*, from an alc. soln. of A and Na. *Potassium*, deliquescent solid. The action of acids gives solid products which are probably polymerized $\text{C}_2\text{H}_4\text{S}$, m. 177–80° and 193–7°. ZnCl_2 or P_2O_5 behaved similarly. Concd. HCl gives β -chloroethyl mercaptan, b_1 125–6°, d_4^{20} 1.225, d_4^{20} 1.203, n_D^{20} 1.5289; it has a marked vesicant action. NaOH quickly decomp. the chloride, giving $(\text{C}_2\text{H}_4\text{S})_n$. By the reaction of A or $\text{PhNHCOOSC}_2\text{H}_4\text{OH}$ with PhCNO there results the compound $\text{PhNHCOOSC}_2\text{H}_4\text{OCONHPh}$, needles, m. 146°.

C. J. WEST

Hydrolysis of β, β' -dichlorodiethyl sulfide. Synthesis of divinyl sulfide and the preparation of a non-vesicant isomeride of β, β' -dichloroethyl sulfide. S. H. BALES AND S. A. NICKELSON. *J. Chem. Soc.* 121, 2137–9(1922).—Hydrolysis of $\text{S}(\text{CH}_2\text{CH}_2\text{Cl})_2$ with 20% EtOH - KOH gave 26% of a light oil, which distils over with the EtOH

and is pptd. by H_2O , b. $85-86^\circ$, d_4^{15} 0.9174. After 48 hrs. the liquid polymerizes to an opaque jelly, somewhat sol. in CS_2 . Hydrolysis with 20% NaOH in 50% EtOH does not give this light oil, but about 2.5% of a heavy oil (cf. Helfrich and Reid, *C. A.* 14, 2486). The light oil may be $S(CH:CH_2)_2$. It adds HCl, giving a clear liquid having a most pungent, objectionable and persistent odor, $C_4H_8Cl_2S$, b₁₀ $58.5-9.5^\circ$, d_4^{15} 1.1972. It appears to be devoid of vesicant properties and decomp. on distn. at atm. pressure between 120° and 145° with evolution of HCl.

C. J. WEST

Betaines. I. Theory of the betaines. PAUL PFEIFFER. *Ber.* 55B, 1762-9 (1922); cf. *Naturwissenschaften* 8, 987 (1920).—The betaines, to which a cyclic structure is quite generally assigned, do not obey the stereochem. laws of ring formation; thus *e. g.*, the trimethylbetaines of *m*- and *p*- $H_2NC_6H_4CO_2H$ are formed just as easily as that of the *o*-acid; similar anomalies are met in the phenol and pyridine betaines, etc., and in certain natural and artificial dyes (galloyanin, rosinone, cyanidine, etc.) which are usually formulated as betaine-like compds. It is now known (see especially Debye and Scherrer, *C. A.* 13, 1415) that in the crystals of salts the lattice points are occupied by ions and not by atoms or mols. and it follows that the individual mols. of salts are composed of ions between which are acting considerable electrostatic forces. Since the betaines, from their general chem. behavior, are nothing but intramol. quaternary NH_4 salts the new view as to the nature of salts must hold for them also; *i. e.*, they have

the structure $R \begin{cases} NMe_3^+ \\ CO_2^- \end{cases}$, the only difference between them and NaCl or NaOAc being

that in the latter the ions are sepd. while in the betaines they are united through chains of atoms. This formulation shows that betaine formation involves no ring closure; the elec. polar charges will, to be sure, mutually attract each other but how near to each other they will approach will depend very materially on the configuration of the mol. These same views can be applied directly to the NH_2 acids (cf. in this connection Langmuir, *C. A.* 14, 1481). The assumption of a dipolar nature for NH_2 acids and betaines explains the unusually high m. ps. and slight solubilities in org. solvents of these compds. According to Reis (*C. A.* 14, 2119) and others, ionic and mol. lattice structures, *i. e.*, those in which the lattice points are occupied resp. by ions and by mols. capable of independent existence, are to be sharply distinguished from each other. In the former, corresponding to the crystals of salts, the strong electrostatic attractive forces of the ions produce extraordinarily stable formations with high m. ps. and slight solubilities in org. solvents, while in the mol. lattice structures, corresponding to the crystals of org. (nonsalt-like) compds., the crystal-structure forces are comparable to the affinity forces between individual mols. in org. mol. compds., *i. e.*, they are much less intense than the electrostatic forces between ions, and the crystal structures are therefore relatively much less firm and the substances are characterized by low m. ps. and high solubilities. The same reasoning applies to the salts of bivalent metals with di- CO_2H acids. The following paper gives the results of the first of a series of exptl. investigations undertaken to test the above views. **II. Betaines of the cinnamic acid series.** PAUL PFEIFFER AND GERHARD HAEFFELIN. *Ibid* 1769-88.—It is characteristic of the *trans*-cinnamic acids that the Ph and CO_2H groups, owing to their *trans*-positions, cannot combine, either directly or through other atoms, to form a ring and the fact that, as described below, they readily yield betaines confirms the views given above as to the structure of the betaines. *p*- $Me_2NC_6H_4CHO$ (5.6 g.) refluxed 5 hrs. with 0.92 g. Na ribbon in 40 g. AcOMe, treated with 0.9 g. more of Na and boiled another 3 hrs. gives 6.7 g. *methyl trans-p*-dimethylaminocinnamate, golden yellow leaflets from EtOH- H_2O (1:1), m. $135-8^\circ$; *perchlorate*, prisms, m. $169-70^\circ$, deflagrates on Pt, loses $HClO_4$ in contact with H_2O . Free acid (A) (0.75 g. from 1 g. of the ester heated 2 hrs. on the H_2O bath with an excess of concd. HCl), golden yellow leaflets from alc., m. 220° ; *perchlorate*, m.

196–7°. *Ethyl ester* (0.6 g. from 1 g. of the acid in 10 cc. alc. treated 3 hrs. on the H₂O bath with HCl gas and allowed to stand overnight), golden yellow leaflets from 50% alc., m. 76–8°. *Methyl ester methiodide* (0.8 g. from 0.5 g. of the ester treated with enough MeI to form a thick magma and heated 12 hrs. in a sealed tube at 100°), yellowish leaflets from alc., m. 174–6° on slow, 186° on rapid heating; 1.2 g. in H₂O shaken 4 hrs. with an excess of moist Ag₂O (from 1.2 g. AgNO₃ and 0.4 g. KOH) gives 60–70% of *trans-p-aminocinnamic acid trimethylbetaine*, ⁺Me₃NC₆H₄CH : CHCOO⁻, leaflets with 0.5 H₂O from abs. alc., decomps. 214–20°, deliquesces in the air, easily sol. in H₂O with almost neutral reaction, does not lose its 0.5 mol. of H₂O *in vacuo* over P₂O₅ after weeks at room temp. but at the temp. of boiling PhMe it gradually decomps., becoming yellowish and then reddish brown; *hydrochloride*, C₁₂H₁₆O₂NCl, leaflets from concd. HCl, turns brown 215°, softens 220°, m. 240° (decompn.), loses part of its HCl on recrystn. from alc.; *hydrobromide*, rhombic crystals with 1 H₂O, turns brown 210°, m. 225–30° (decompn.), loses some HBr and becomes dull on too long drying over soda-lime; *hydriodide*, from A heated 30 hrs. at 100° with an excess of MeI or from the betaine rubbed with aq. HI, yellow leaflets from alc., m. 190–1°; *perchlorate*, fine needles difficultly sol. in H₂O (with or without HClO₄) but immediately dissolving on addn. of NH₄OH; the isomeric salt of the Me ester of A (see above) seps. from dil. HClO₄ in broad needles easily sol. in dil. HClO₄, immediately turned turbid by pure H₂O and converted into the free ester by aq. NH₃. That A is indeed a *trans*-compd. was shown by its synthesis in the following way: *trans-p-nitrocinnamic acid*, m. 285–6°, obtained from ordinary cinnamic acid by treatment with fuming HCl (a reaction which has been shown not to involve any change in configuration; cf. C. A. 8, 2722), can be obtained more easily by direct condensation of *p*-O₂NC₆H₄CHO with anhyd. NaOAc (13 g. from 11 g. of the aldehyde); FeSO₄·NH₄OH reduce it to the NH₂ acid, 6.4 g. of which, allowed to stand 12 days in a sealed tube in MeOH suspension with 4.8 g. NaOH and 20 g. MeI, gave 2 g. A, further identified as such by conversion into the Me and Et esters. *trans-p-Me₃NC₆H₄CH : CBrCO₂Me*, m. 96°, was obtained in 4 g. yield from 10 g. of the Me ester of A by Weil's method (C. A. 3, 904) who assumed, without proof, that the Br is in the *p*-position, nor did P. and H. ever succeed in obtaining the intermediate dibromide in cryst. form; the free acid, from the ester by evapn. with concd. HCl, green-yellow leaflets from AcOH, m. 175–6°, sol. in aq. NH₃ with yellow color, in HCl without color, decomps. on long standing (W., who prepd. the acid by sapon. with alc. KOH, gives the m. p. as 165°). The ester (2 g.) heated 20 hrs. at 100° with excess of MeI gives 3.1 g. *methyl trans-p-dimethylanino-α-bromocinnamate methiodide*, light yellow leaflets from alc., m. 171–2°, 1.6 g. of which with Ag₂O yields 0.7 g. *trans-p-amino-α-bromocinnamic acid trimethylbetaine*, long needles, softens 218–9°, m. 222° (decompn.); *hydrochloride*, felted needles, turns brown 205°, does not m. 250°; *hydrobromide*, needles, turns brown 190°, does not m. 250°. The configuration of this betaine was not detd. but the analogous Cl compd. was synthesized in such a way as to leave no doubt that it is a *trans*-deriv. From 55 g. PhCHClCHClCO₂H, m. 167°, obtained in 92% yield by Liebermann and Finkenbeiner's method, was obtained 38 g. PhCH : CCICO₂H, sepd. by Sudborough and James' method into the *trans*-acid (20–30 g.), m. 139°, and the *cis*-compd., m. 112–4°. The *trans*-acid with fuming HNO₃ at room temp. yields an equal wt. of *trans-p*-O₂NC₆H₄CH : CCICO₂H, m. 220–4° (*cis*-compd., m. 152–3°), 2 g. of which with FeSO₄·NH₄OH on the H₂O bath gives 1.2 g. of the *trans*-NH₂ acid, turns brown 219°, does not m. 250°; *methyl ester* (1.2 g. from 2 g. of the acid in MeOH with HCl gas on the H₂O bath), light yellow needles from alc., m. 123°, sol. in aq. HCl, gives on evapn. in concd. HCl a substance consisting chiefly of the HCl salt of the acid. Allowed to stand 12 days in a sealed tube in a little MeOH with MeI and NaOH the *trans*-NH₂ acid yields the *hydrochloride*, faintly yellowish needles, darkens 170°, softens around

200°, does not m. 250°, of *trans-p-amino- α -chlorocinnamic acid trimethylbetaine*, needles, turns yellow, then brown, on heating, m. 252-6°; *perchlorate*, leaflets. C. A. R.

Constitution of carbamides. XIV. The decomposition of urea by sodium hypobromite in alkaline solution and an improved procedure for the estimation of urea by this means. E. A. WERNER. *J. Chem. Soc.* 121, 2318-25(1922); cf. *C. A.* 15, 1133.—When urea is decompd. by NaBrO, the N usually recovered is about 8% less than the theoretical. Practically theoretical results may be obtained as follows: CO(NH₂)₂ is added in the usual manner to a small excess of NaBrO, allowed to act 20 min., the vol. of gas accurately read and then expelled from the nitrometer. The liquid is now treated with 1 : 5 H₂SO₄ until the latter shows the permanent presence of Br, allowed to stand 15 min., 30% NaOH added in excess and also a little NaBrO and the N in the CO₂-N mixt. detd. The sum of the 2 vols. of N corresponds to the total CO(NH₂)₂ present. Duggan's results (*J. Am. Chem. Soc.* 4, 175) concerning the suppression of cyanate formation by the formation of the NaBrO *in situ* are confirmed. Méhu (*Compt. rend.* 89, 175) proposed the use of dextrose in the detn. of CO(NH₂)₂. It is shown that the amt. of gas liberated in the 2nd stage is not increased, while in the 1st stage CO is formed, increasing with the amt. of dextrose added. The proportion of N fixed as cyanate was distinctly higher when dextrose was present. Neutral NaBrO does not liberate N from CO(NH₂)₂ in the cyclic form. A change to the configuration HN : C(OH)-NH₂ must precede the decompn., which is no doubt the result of bromination, hydrolysis and oxidation following each other with such great velocity as to be practically simultaneous. The mechanism of the reaction is discussed. C. J. WAST

Thiocyanates and isothiocyanates. XV. The nature of the intramolecular rearrangement of isothiocyanatoacetanilides. A. J. HILL AND E. B. KELSEY. *J. Am. Chem. Soc.* 44, 2357-69(1922); cf. *C. A.* 14, 2929.—It has been shown in earlier papers that the primary products resulting from the action of chloroacetanilides on KCNS are the normal thiocyanatoacetanilides which rearrange into labile pseudothiohydantoins and the latter into stable isomers. Recently Beckurts and Frerichs (*C. A.* 10, 888) stated that KCNS with certain chloroanilides gives as primary products unstable *isothiocyanates* which rearrange into *normal thiocyanates* and the latter into arylthiohydantoins. Using the method described in the earlier paper, H. and K. have converted B. and F.'s chloroanilides successively into the corresponding primary amines, dithiocarbamates, carbethoxydithiocarbamates and finally the isothiocyanates and have found that the latter are so unstable that they rearrange immediately into normal 2-thiohydantoins. B. and F. could therefore not have been dealing with isothiocyanates as the primary products of their reactions. *Aminoacet-p-chloroanilide* (A), obtained in 65 g. yield from 100 g. ClC₆H₄NHCOCH₂Cl in 2.5 l. alc. NH₃ (satd. at 10°) allowed to stand 6 days at room temp., stout needles with 1 H₂O, m. 81° and, anhyd., 64°; there is also formed *diglycolamidic di-p-chlorophenylamide*, (ClC₆H₄NHCOCH₂)₂NH, long needles from alc., m. 170-1°. *Carbethoxyaminoacet-p-chloroanilide* (B) (10 g. from 8 g. A in C₆H₆ with 1.33 mols. ClCO₂Et and somewhat more than 1 mol. of 2 N NaOH), fine needles from 95% alc., m. 198°. *Benzoylaminoacet-p-chloroanilide* (7 g. from 8 g. A in C₆H₆ with 1.33 mols. BzCl and a slight excess of 2 N NaOH), m. 217-8°. *Aminoacet-p-chloroanilide dithiocarbamate* (C) (37 g. from 40 g. A in 95% alc. treated at 30° with 123 g. CS₂), light salmon-colored plates from H₂O, begins to decomp. 125-30°, turning red and giving off H₂S, m. 155° when heated rapidly; when 30 g. in 350 cc. Et₂O is allowed to stand 60 hrs. with 9.7 g. ClCO₂Et, there remains 24 g. of an Et₂O-insol. residue consisting of A, HCl, unchanged C and B, while the Et₂O soln. on evapn. gives 11 g. light yellow crystals, m. 103°, consisting of *carbethoxyaminoacet-p-chloroanilide dithiocarbamate* (contaminated with some B), 9 g. of which, heated to 140-5° under 40 mm., gives COS or CS₂, 1 g. EtOH and 4 g. *1-p-chlorophenyl-2-thiohydantoin* (D), pale

yellow fluffy needles from 95% alc., m. 225-7° (decompn.), desulfurized by heating 3 hrs. on the H₂O bath with aq. ClCH₂CO₂H to *1-p-chlorophenylhydantoin* (E) (37% yield), needles from alc. or H₂O, m. 174°, also obtained by allowing B to stand 3.5 days with 1 mol. KOH in 95% alc. C with 0.5 mol. aq. HgCl₂ gently heated until the evolution of H₂S ceases gives D. *1-p-Chlorophenyl-2-thio-4-benzalhydanitoin*, obtained quant. from D gently boiled 4 hrs. with 2 mols. BzH in NaOAc-AcOH, long fluffy pale yellow needles from alc., m. 257°, gives with 1 mol. NaOEt and 1 mol. BzCl in abs. alc. 55% of *1-p-chlorophenyl-1-benzylmercapto-4-benzalhydanitoin*, pale lemon-yellow needles from alc., m. 176.5°. *1-p-Chlorophenyl-4-benzalhydanitoin*, obtained in 38% yield from E with BzH, NaOAc and AcOH, long pale yellow needles from alc., m. 274°. *Aminoacet-p-anisidide* (yield, 73%), silky needles from 25% alc., m. 98-9°. *Diglycolamidic di-p-methoxyphenylamide*, plates or long flat needles from 30% alc., m. 143°; in 1 expt. there was also obtained a small amt. of *triglycolamidic tri-p-methoxyphenylamide*, heavy plates from alc., m. 192-3°. *Carbethoxylaminoacet-p-anisidide*, plates from alc., m. 154°; yields, almost quant. *Aminoacet-p-anisidide dithiocarbamate* (F) (52 g. from 50 g. of the amine), broad thin blades from alc., reddens 130°, decomp. 140-5° (H₂S evolution); 50 g. gives 26 g. of the impure *carbethoxy derivative* (G) which at 130° under 40 mm. yields S compds., 81% EtOH and 85% *1-p-methoxyphenyl-2-thiohydantoin* (H), light yellow needles from alc., m. 207-9°, also obtained from F with HgCl₂, gives with ClCH₂CO₂H 80% of *1-p-methoxyphenylhydantoin*, needles from 20% alc., m. 208°, also obtained in 87% yield from G. *1-p-Methoxyphenyl-2-thio-4-benzalhydanitoin* (5 g. from 4 g. H); yellow plates from alc., m. 203°; *2-benzylmercapto compound*, slender light yellow needles from alc., m. 174° (yield, quant.). *1-p-Methoxyphenyl-4-benzalhydanitoin* (yield, 84%), long pale yellow needles from alc., m. 238°. *Aminoacet-m-toluidide*, needles with 1 H₂O, m. 74-5°, and, anhyd., 54-5°, reacts alk. to litmus, absorbs CO₂ from the air, forms stable salts with acids; yield, 80-4%. *Diglycolamidic di-m-tolylamide*, needles or plates from 50% alc., m. 136°. *Benzoylaminoacet-m-toluidide* (7 g. from 5 g. of the amine), needles from alc., m. 186°. *Carbethoxylaminoacet-m-toluidide*, prismatic crystals from C₆H₆, m. 103°. *Aminoacet-m-toluidide dithiocarbamate* (yield, 85%), heavy granular crystals from AcOEt, becomes slightly pink on standing, decomp. 138° (H₂S evolution), decomp. quite rapidly in hot H₂O. *Carbethoxylaminoacet-m-toluidide dithiocarbamate* (I) (80 g. from 100 g. of the NH₂ compd.), yellow needles from alc., decomp. 113°, is rapidly decompd. by boiling H₂O, yields at 120° under 30 mm. S compds., 83% EtOH and 47% *1-m-tolyl-2-thiohydantoin*, bright lemon-yellow needles from alc., m. 187°, also obtained from the NH₂ compd. with HgCl₂ and desulfurized by ClCH₂CO₂H in 64% yield to *1-m-tolylhydantoin*, needles from 25% alc., m. 123°, also obtained in 4 g. yield from 12 g. I. *1-m-Tolyl-2-thio-4-benzalhydanitoin*, slender needles from alc., m. 183° (yield, 91%); *2-benzylmercapto compound*, seps. from alc. in long silky needles changing on standing or recrystg. into thin yellow plates, both forms melting at 145°. *1-m-Tolyl-4-benzalhydanitoin*, broad pale yellow needles from alc., m. 214°; yield, 56%. On attempting to recryst. (*p*-ClC₆H₄NHCOCH₂)₂NH (J) from Me₂CO there sepd. a substance m. 250-1° which could not be crystd. owing to its insol. in practically all solvents but whose compn. agreed fairly well with the formula 2 J·Me₂CO. A similar compound (found, 13.41-13.47% N), large blunt needles from Me₂CO, m. 166-7°, was obtained when (PhNHCOCH₂)₂NH was boiled a short time with Me₂CO.

C. A. R.

Potassium azidodithiocarbonate. A. W. BROWNE AND A. B. HOEL (with notes on crystallography by A. C. GILL). *J. Am. Chem. Soc.* **44**, 2315-20 (1922); cf. *J. Am. Chem. Soc.* **44**, 2116; Sommer, C. A. **10**, 342.—Potassium azidodithiocarbonate is prepd. by heating KN₃ in H₂O with somewhat more than 1 mol. CS₂ at 40° until the CS₂ disappears, concg. *in vacuo* over P₂O₅ almost to satn. and cooling in ice; it seps. in anhyd.

crystals of quite variable habitus, with tabular development with 4- or 6-sided outlines most common, deliquesce rather rapidly in the air; about 4.5 parts dissolve in 1 of H_2O ; the salt is rather sensitive to shock; on slow heating it begins to decomp. about 128° and is converted quant. into $KSCN + S + N_2$; in air it explodes spectacularly, chiefly according to the equation $2KSCN_3 + 5O_2 = K_2S + 3SO_2 + 2CO_2 + 3N_2$; the dry salt and aq. solns. are quite stable below 10° ; at somewhat higher temps. the aq. solns. give $KSCN$, S and N_2 ; the salt gives $(SCSN_3)_2$ with various oxidizing agents and on anodic oxidation.

C. A. R.

Mechanism of guanidine formation in fused mixtures of dicyanodiamide and ammonium salts. J. S. BLAIR AND J. M. BRAHAM. *J. Am. Chem. Soc.* 44, 2342-52 (1922).—Dicyanodiamide was fused with NH_4NCS and with NH_4NO_3 and biguanide nitrate with NH_4NO_3 , and samples of the mixt. before, at various intervals during, and after the fusions were analyzed for total N , NH_4 , guanidine and biguanide and qual. tested for cyanamide. Qual. expts. were also made on fused mixts. of dicyanodiamide with $(NH_4)_2SO_4$ and with NH_4Cl . The results show that the mechanism of the reaction is to be represented by the scheme $H_2NC(:NH)NHCN + NH_3.HX \rightarrow H_2N(:NH)C(:NH)NH_2.HX \xrightarrow{NH_3.HX} 2H_2NC(:NH)NH_2.HX$. The mechanism previously suggested, viz. $(H_2NCN)_2 \rightarrow 2H_2NCN \xrightarrow{NH_3.HX} H_2NC(:NH)NH_2.HX$ (cf. Werner and Bell, C. A. 15, 371) cannot be directly verified experimentally. The statement that biguanide salts are formed in such mixts. by de-ammonation of 2 mols. of guanidine salt (Davis, C. A. 16, 410) is shown to be very doubtful; the biguanide salt is an intermediate product in the formation of the guanidine salt in such fused mixts. and is not a product of a side reaction. The reactions taking place in such fused mixts. cannot be offered as evidence against the cyanoguanidine structure for dicyanodiamide and are rather in entire accord with it.

C. A. R.

On oxidation of tertiary hydrocarbons. P. A. LEVENE AND F. A. TAYLOR. *J. Biol. Chem.* 54, 351-62 (1922); cf. Levene and Cretcher, C. A. 12, 1545.—The hydrocarbons were prepd. from substituted malonic esters by the following series of reactions: $R'R'C(CO_2R)_2 \rightarrow R'R'C(CO_2H)_2 \rightarrow R'R'CHCO_2H \rightarrow R'R'CHCO_2R \rightarrow R'R'CHCH_2OH \rightarrow R'R'CHCH_2I \rightarrow R'R'CHMe$. The following compds. were prepd. and are described. *Diethyl ethylmalonate*, b. $206-8^\circ$. *Diethyl butylethylmalonate*, b. $128-9^\circ$, d_4^{20} 0.9646, n_D^{20} 1.4284. *Butylethylmalonic acid*, m. 115° . *2-Ethylhexylic acid*, b. $228-9^\circ$. *Ethyl 2-ethylhexylate*, b. $189-91^\circ$, d_4^{20} 0.8628, n_D^{20} 1.4128. *2-Ethylhexanol*, b. $181-3^\circ$, d_4^{20} 0.8328, n_D^{20} 1.4328. *2-Ethylhexyl iodide*, b. $89-90^\circ$. *3-Methylheptane*, b. $120-2^\circ$, d_4^{20} 0.7069, n_D^{20} 1.3980. *Diethyl 1-methylheptylmalonate*, b. $157-8^\circ$, d_4^{20} 0.9496, n_D^{20} 1.4324. *1-Methylheptylmalonic acid*, could not be crystd. *3-Methylnonylic acid*, b. $147-8^\circ$, d_4^{20} 0.9012, n_D^{20} 1.4342. *Ethyl 3-methylnonylate*, b. 115° , d_4^{20} 0.8653, n_D^{20} 1.4240. *3-Methylnonanol*, b. $103-3.5^\circ$, d_4^{20} 0.8342, n_D^{20} 1.4361. *3-Methylnonyl iodide*, b. 115° , d_4^{20} 1.2515. *3-Methylnonane*, b. $165-6.5^\circ$, d_4^{20} 0.7354, n_D^{20} 1.4126. *2-Butylhexanol*, b. $210-2^\circ$. *2-Butylhexyl iodide*, b. $115-7^\circ$. *5-Methylnonane*, b. $164-6^\circ$, d_4^{20} 0.7319, n_D^{20} 1.4116. *4-Butyloctanol*, b. $127-30^\circ$. *4-Butyloctyl iodide*, b. $145-6^\circ$. *5-Propylnonane*, b. $204-5^\circ$, d_4^{20} 0.7559, n_D^{20} 1.4228. *Diethyl butylmalonate*, b. 122° , d_4^{20} 0.9745, n_D^{20} 1.4222. *Diethyl butylheptylmalonate*, b. $177-8^\circ$, d_4^{20} 0.9518, n_D^{20} 1.4366. *Butylheptylmalonic acid*, m. 117° . *2-Butylnonylic acid*, b. 179° , d_4^{20} 0.8860, n_D^{20} 1.4403. *5-Methyldecane*, b. $225.5-7.0^\circ$, d_4^{20} 0.7576, n_D^{20} 1.4244. Of the 5 hydrocarbons prepd., only 5-methylnonane was oxidized by $KMnO_4$ and KOH at 37° for 16 hrs. After destroying the excess of $KMnO_4$ with H_2O_2 , filtering, acidifying and distg. in steam, the volatile acids were sepd. by Crowell's method (C. A. 12, 574). From 20 g. of 5-methylnonane there were obtained 1.5 g. Ag butyrate (pure) and 1.4 g. AgOAc, contaminated with

AgO_2CH . Although BuOH is oxidized by alk. KMnO_4 the amt. of HOAc so formed is, apparently, not sufficient to account for the HOAc obtained from the oxidation of the 5-methylnonane.

I. GREENWALD

Quantitative reduction by hydriodic acid of halogenated malonyl derivatives.

II. The sym-tetrasubstituted amides of bromo- and chloromalonic acid. R. W. WEST. *J. Chem. Soc.* 121, 2196-2202(1922); cf. *C. A.* 15, 2070.—In extending the work to the sym-tetrasubstituted amides, it has been found that substitution of Br for H in CHCl_2 or AcOH only takes place in the CH_2 group of the malonyl radical. *Bromomalonomethyl-anilide*, $\text{CHBr}(\text{CONMePh})_2$, stout prisms from $\text{CHCl}_2\text{-EtOH}$, m. 198° . *Bromomalonomethylbromoanilide*, by the further action of Br, stout prisms, m. 172° . *Chloromalonomethyl-anilide*, prisms, m. 187° . *Bromomalontetraphenylamide* (A), $\text{CHBr}(\text{CONPh})_2$, prisms, m. 201° . *Bromomalontetra[bromophenyl]amide*, small needles, m. 169° . *Chloromalontetraphenylamide*, by the action of Cl upon $\text{CH}_2(\text{CONPh})_2$ or upon A, prisms, m. 204° . *Bromomalontetrabenzylamide* (B), prisms, m. 137° . *Chloro derivative* (C), small needles, m. 119° . The action of Cl upon B or C gives the *dichloro derivative*, prisms, m. 138° . *Chloromalon-p-bromoanilide*, by the action of Cl in AcOH upon $\text{CH}_2(\text{CONHC}_6\text{H}_4\text{Br})_2$, thin prisms, m. 239° . This reacts with Cl to form the *dichloro derivative*, needles, m. 184° , and with Br to form the *chlorobromo derivative*, prisms, m. 162° . *Chlorobromomalondithylamide*, by the action of Cl upon $\text{CHBr}(\text{CONHEt})_2$ or $\text{CBr}_2(\text{CONHEt})_2$, needles, m. 122° . *Dichloromalondimethylamide*, needles, m. 158° . *Chlorobromo derivative*, prisms, m. 130° . The question of "strain interference" in the formation of these compds. is discussed.

C. J. WEST

Addition of ethyl sodiocyanoacetate and ethyl sodiomalonate to ethyl muconate.

E. H. FARMER. *J. Chem. Soc.* 121, 2015-22(1922).— $\text{EtO}_2\text{CCH:CHCH:CHCO}_2\text{Et}$ (A) adds Br at the 1,2-position (*C. A.* 16, 3085). Since the muconic system follows the 1,4-rule of H addition, it is desirable to study the addition of unsym. compds. to A. In the 2 compds. studied, the addns. are of the 1,3-type. *Ethyl Δ^2 -butene- α,δ -dicarboxylate- β -cyanoacetate* (B), from A and $\text{NCCNNaCO}_2\text{Et}$ in Et_2O contg. a little abs. EtOH , viscous, pale yellow oil, b_{20} 210° but decomp. above this pressure. There action of A and $\text{CHNa}(\text{CO}_2\text{Et})_2$ gives the *β -malonate* (C), b_{11} 215° . A small amt. of the *triethyl hydrogen ester* is formed in this reaction. Hydrolysis of B with H_2SO_4 gives *2,6-dihydroxypyridine-4-propionic acid*, pale, brownish yellow flakes, decomp. 257° ; its solns. turn green or purple on standing. The *sulfate* and *hydrochloride* form microneedles readily sol. in cold H_2O . A 2nd product of the hydrolysis, upon esterification, gives *ethyl Δ^2 -butene- α,δ -dicarboxylate- β -acetate* (D), b_{10} $195\text{--}205^\circ$. The free acid (E) is obtained by the hydrolysis of D or B, colorless aggregates, m. 179° . *Silver salt*, curd-like ppt. Boiling AcCl gives the *anhydride*, flattened needles, m. 116° . *Sodium salt* of C, (F), pale yellow, very hygroscopic powder. The acidification of the aq. soln. of this salt with the theoretical amt. of dil. HCl gave a 2nd modification of E, cryst. powder, m. 152° . The oxidation of E or F by KMnO_4 gave only $(\text{CO}_2\text{H})_2$ or $(\text{CH}_3\text{CO}_2\text{H})_2$. No trace of tricarballic acid could be detected. The oxidation of B gave $(\text{CO}_2\text{H})_2$ and $\text{HO}_2\text{CCH}_2\text{CH}_2\text{COCH}(\text{CN})\text{CO}_2\text{Et}$.

C. J. WEST

Ethyl α -cyano- β -methylglutaconate and its methyl homologs. EDWARD HOPE. *J. Chem. Soc.* 121, 2216-23(1922).—Expts. are recorded which confirm Thorpe's corrected view on the constitution of $\text{EtO}_2\text{CC}(\text{CN})\text{:CMeCHMeCO}_2\text{Et}$ (*C. A.* 7, 2927). The action of concd. NH_4OH upon $\text{EtO}_2\text{CCMe}(\text{CN})\text{:CMe:CHCO}_2\text{Et}$ (A'), gives $\text{H}_2\text{NCMe:CHCO}_2\text{Et}$, m. $20\text{--}1^\circ$, and a product which could not be purified but which, on boiling with NaOH , splits off NH_3 and gives 6-hydroxy-2-keto-4-methyl-2,3-dihydropyridine-3-carboxylonitrile (Guareschi, *Mem. Accad. Sci. Torino* 46, 1(1896)). The action of concd. NH_4OH upon $\text{EtO}_2\text{CCH}(\text{CN})\text{:CMe:CMCO}_2\text{Et}$ (A) for 24 hrs. causes the disappearance of the oil and the appearance of $\text{H}_2\text{NCMe:CMCO}_2\text{Et}$, m. $50\text{--}1^\circ$, and a substance,

decomp. about 320° which, on heating with alkali, splits off NH_3 and gives a compd. m. 276° , which is the 4,5-Me₂ deriv. described by Guareschi. $\text{EtO}_2\text{CC}(\text{CN})\text{:CMe-CHMeCO}_2\text{Et}$ (B) reacts in the same way with NH_4OH as A, the probable explanation being that B undergoes an isomeric change, with shift of the double bond, into A. This change may be effected by shaking the ester (B) with EtONa for 0.5 min., quickly pouring into cold dil. HCl and extg. with Et_2O . The action of H_2O upon A' at $170\text{--}80^\circ$ gave EtOH , AcMe and $\text{NCCH}_2\text{CO}_2\text{Et}$. The action of H_2O upon A or B gave EtOH , MeEtCO and a mixt. of $\text{NCCH}_2\text{CO}_2\text{Et}$ and $\text{AcCHMeCO}_2\text{Et}$. C. J. WEST

Addition of hydrogen cyanide to derivatives of glutaconic acid. I. The addition of hydrogen cyanide to ethyl α -cyano- β -methylglutaconate and its homologs. EDWARD HOPE AND WILFRED SHELTON. *J. Chem. Soc.* 121, 2223-35(1922); cf. preceding abstr.— $\text{EtO}_2\text{CCH}(\text{CN})\text{CMe}(\text{CN})\text{CH}_2\text{CO}_2\text{Et}$ (A) (Hope, *C. A.* 6, 3410) can be prepd. in 80% yield by treating $\text{EtO}_2\text{CCH}(\text{CN})\text{CMe}:\text{CHCO}_2\text{Et}$ (B) in alc. with KCN and, after cooling, with 1.5 mols. 20% HCl . The action of NH_3 leads to the same products as with B (see above). An attempt was made to increase the ease of prepn. and yield by condensing $\text{CNCHNaCO}_2\text{Et}$ and $\text{MeC}(\text{OH})(\text{CN})\text{CH}_2\text{CO}_2\text{Et}$, but the yield was the same as above (40%). Ethyl α,β -dicyano- β -methylbutane- α,γ -dicarboxylate, b₂₀ $200\text{--}6^\circ$. NH_3 gives $\text{H}_2\text{NCH}:\text{CMeCO}_2\text{Et}$, and Guareschi's compd. Hydrolyzed by boiling with concd. HCl for 12 hrs. gives α,β -dimethyltricarballic acid (C), m. $165\text{--}7^\circ$ (forming an anhydride?). The methyl ester, b_m 162° . Ethyl β,γ -dicyano- γ -methylbutane- β,δ -dicarboxylate, b₁₁ $196\text{--}7^\circ$. When hydrolyzed with 40% H_2SO_4 it yielded a substance which on treatment with MeOH-HCl , gave a compound $\text{MeCH.CO.NH.CO.CH}_2\text{CMeCO}_2\text{Me}$,

b₁₁ $219\text{--}24^\circ$, m. $136\text{--}7^\circ$. Hydrolysis with concd. HCl in a sealed tube at 175° gave C. Ethyl β,γ -dicyano- γ -methylpentane- β,δ -dicarboxylate, b₁₁ $202\text{--}7^\circ$. Hydrolysis, followed by esterification, gave methyltrimethyltricarballic acid, b₂₄ $164\text{--}7^\circ$. The free acid apparently does not exist as such, for hydrolysis of the ester gave the anhydride, m. $188\text{--}90^\circ$. C. J. WEST

Diacylacetone. J. N. COLLIE AND A. A. B. REILLY. *J. Chem. Soc.* 121, 1984-7 (1922); cf. *C. A.* 16, 96.—Diacylacetone (A) does not behave like a triketone nor as a compd. contg. ordinary HO groups. All that can be said at present is that the atoms are linked together probably in a ring or rings. A is best prepd. by boiling dehydracetic acid with concd. HCl until evolution of CO_2 ceases; the HCl is removed in vacuum, the residue neutralized with NaOH , excess of $\text{Ba}(\text{OH})_2$ added, the mixt. brought to the b. p., the ppt. collected, decompd. with HCl , shaken out with CHCl_3 and the residue fractionated. A, b₁₀ 121° , has n_D^{20} of 1.4890 when 1st distd., which rapidly changes to 1.4988 and becomes const. at 1.4930 when the substance crysts. In 1 expt. a residue was obtained, giving the compound $\text{C}_{14}\text{H}_{14}\text{O}_4$ (B), m. $181\text{--}5^\circ$; this gives a deep green color with concd. H_2SO_4 , and with NaOH a Na salt from which acid ppts. a substance m. $125\text{--}30^\circ$. Et_3NH , Et_3N and $\text{C}_6\text{H}_{11}\text{N}$ and A gave a compound $\text{C}_{14}\text{H}_{14}\text{O}_4$, m. 181° (same as B?). Me_2SO_4 , CH_3N_3 , and PCl_5 in CHCl_3 gave dimethylpyrone. ZnEt_2 , BzH and HCHO were without action. Et_3N and I in CHCl_3 gave the compd. $\text{C}_7\text{H}_7\text{O}_2\text{I}$ (*C. A.* 16, 96). PhNHNH_2 and A give the compound $\text{C}_{19}\text{H}_{20}\text{N}_2$, m. 152° (cf. Feist, *Ann.* 257, 278). The semicarbazone (B), $\text{C}_8\text{H}_7\text{ON}_4$, forms long silky needles, m. 203° . Hydrochloride, with 1 H_2O , loses both H_2O and HCl when heated to 140° . Sulfate. Oxalate.—Sodium salt, silky needles, the soln. of which is strongly alk. Barium salt.—No ppt. is formed with Cu , Pb or Fe salts. B can be boiled with 90% H_2SO_4 without decompn., but concd. NaOH causes the slow evolution of NH_3 . Heated with Zn dust in an atm. of H_2 , lutidine (?) is formed. With an excess of HNO_3 a bright green compound, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_6(\text{NO})\text{H}_2\text{O}$, seps. Urea and A give a compound, $\text{C}_8\text{H}_7\text{O}_4\text{N}_2$, shining plates, m. $267\text{--}70^\circ$. NH_4OH and A form a deliquescent liquid which decomp. when heated. C. J. WEST

Interchange of alcohol radicals in esters. II. AKIRA SHIMOMURA AND J. B. COHEN. *J. Chem. Soc.* 121, 2051-9(1922); cf. C. A. 16, 2502.—The acid nature of an alkyl ester seems to promote the interchange of groups. The introduction of the following groups generally helps the reaction: Ph, Ac, AcO, PhO, CO₂H, NO₂. Halogens do not materially affect the interchange. In some cases a double bond does. Most of the esters of α -ketonic acids undergo interchange, due, undoubtedly, to the presence of the CO group in the α -position to the CO₂H group. The HO group is not favorable to the interchange. In the case of esters of BzH derivs., *o*- and *p*-compds. behave similarly but differ from the *m*-compd. The following new esters are described: *L*-Menthyl acetylpyruvate, *b*₁₂ 185-92°, $[\alpha]_D^{18}$ -72.3°; monoacetylmalonate, long needles, m. 58°, $[\alpha]_D^{19}$ -77.5°; phenoxy-malonate, microneedles, m. 96° $[\alpha]_D^{17}$ -55.5°; ethoxymethylenemalonate, *b*₁₀ 215-21°, $[\alpha]_D^{20}$ -39.6°; hydrogen succinate, prisms, m. 57-9°, $[\alpha]_D^{17}$ -61.0°. C. J. WEST

Oxime of mesoxamide (isonitrosomalonalonamide) and some allied compounds. IV. The ethers of isonitrosomalonalonamide, isonitrosomalondimethylamide and isonitrosomalondibenzylamide. A. G. RENDALL AND M. A. WHITLEY. *J. Chem. Soc.* 121, 2110-9(1922); cf. *J. Chem. Soc.* 83, 24.—Only those isonitroso derivs. of the substituted malonalonamides that exhibit isomerism yield isomeric forms of ethers, for in the 3 cases studied, isonitrosomalonalonamide, which exists in a colorless and a yellow form, is the only one to yield a colorless and a yellow ether. The action of alkyl iodide and Ag₂O gave only colorless ethers. Isonitrosomalonalonamide: methyl ether, stout prisms, m. 194°; ethyl ether, wheat-sheaf clusters of thin prisms, m. 106°; isopropyl ether, felted masses of very thin needles, m. 170°; propyl ether, thin, prismatic needles, m. 156°; butyl ether, thin prisms, m. 138.5°. The action of CH₃N₃ in Et₂O gave the yellow methyl ether, m. 144°, decomp. 150°. Repeated crystn. from alc. gave the colorless form, m. 194°. Me₂SO₄ gave only the colorless ether. Isonitrosomalondimethylamide: methyl ether, stout prisms, m. 131°; ethyl ether, rhombic prisms, m. 133°; isopropyl ether, stellate clusters of flattened prisms, m. 128°; *n*-propyl ether, thin prismatic needles, m. 94°; *n*-butyl ether, rhombic prisms, m. 66°. Isonitrosomalondibenzylamide: methyl ether, slender acicular prisms, m. 83.5°; ethyl ether, small prisms, m. 73.6°. Isonitrosomalonalonamide and its esters are quant. reduced to aminomalonalonamide, brilliant, flattened prisms, m. 146°. C. J. WEST

Methylation of xylose. ALBERT CARRUTHERS AND E. L. HIRST. *J. Chem. Soc.* 121, 2299-308(1922).—The study of the compn. of various types of cellulose necessitates the study of methylated derivs. of pentoses, since esparto cellulose has been shown to contain 20% xylan and straw cellulose some 19% pentosan. Xylose was methylated by the 2 known methods. In the 1st Me₂SO and NaOH was used at 30° until reducing action had disappeared, the remainder of the reagents added at 70° and the reaction completed by boiling for half an hour, giving a product consisting of long needles, m. 35-40°. Methylation was completed by treatment with MeI and Ag₂O, giving trimethylmethylyxyloside, the β -form being obtained by crystn. of the distd. product from petrol. ether, m. 46-8°, n_D^{24} 1.4316, n_D^{25} 1.4350, $[\alpha]_D$ -66.6° in MeOH (c 1.160), -64° in EtOH (c 1.1), -67° in H₂O (c 1.114). The equil. value of the sp. rotation after treatment with acidified MeOH at 100° for 8 hrs. was 49.5° (c 1.15). In the 2nd expt., xylose was treated with 0.25% acidified MeOH (formation of methylyxyloside), most of the β -form crystd. out and the resulting sirup treated with MeI and Ag₂O (5 times). The resulting product was a mobile sirup, *b*₁₂ 115-8°, n_D^{25} 1.4410, n_D^{29} 1.4380, $[\alpha]_D$ 86° in MeOH (c 2.534). The equil. value of the sp. rotation was found to be 50.4°. α -Trimethylxylose is obtained in 50% yield by the hydrolysis of the xyloside with 8% aq. HCl, large prisms of characteristic shape and appearance, m. 87-90°, $[\alpha]_D$ 20° in H₂O (c 1.50); mutarotation was so rapid that the initial value could not be read; in EtOH, initial 74°, final 21° (c 0.879); in MeOH, final, 20.1° (c 1.095). Acid rapidly catalyzes

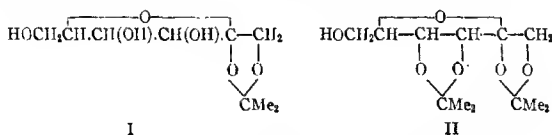
the mutarotation in EtOH, NH₃ very slowly. Furfural derivs. were formed in quantity in the hydrolysis. The hydrolysis of the α -xyloside by means of 5% H₂SO₄ for 7 hrs. on a H₂O bath gave a viscous sirup, slightly acid in reaction, contained considerable ash, had $[\alpha]_D -6.4^\circ$ and 32.3% MeO. The rate of condensation of trimethylxylose with acidified MeOH is much slower than in the hexose series. This would seem to indicate a great stability of structure, while the transformation to furfural appears to show the reverse to be the case.

C. J. WESS

γ -Methylfructoside. R. C. MENZIES. *J. Chem. Soc.* 121, 2238-47 (1922).—Using as a solvent pure MeOH free from AcMe and carefully dried, the optical rotations of solns. contg. not more than 5% fructose change sign in about 20 min. from the time of addn. of HCl and attain max. positive values in little more than 0.5 hr. The addn. of 1% H₂O is sufficient to inhibit the change in sign of the optical rotation otherwise observed. γ -Methylfructoside was prepd. by the reaction of 7 g. fructose in 350 cc. MeOH-HCl (acidity 0.5%) for 32 min.; the acid was neutralized with MeONa, the solvent removed by distn. and the new product extd. by AcOEt; it forms a hygroscopic sirup with $[\alpha]_D$ of 25.2° in AcOEt and 26.6° in H₂O. It does not reduce Fehling soln. on immediate boiling, but does after standing 6 hrs. A 0.927% soln. containing 0.033% HCl at 20° showed a steady decrease in rotation from 22.06 to -64.26° after 27 days. Under similar conditions β -methylfructoside is unattacked. Identification of the ketose residue was made by comparison of the derived tetramethylfructose and tetramethylmethylfructoside, the products being the same as those obtained from inulin and sucrose.

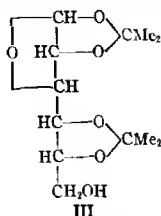
C. J. WESS

The constitution of acetone derivatives of glucose and fructose. J. C. IRVING AND JOCELYN PATTERSON. *J. Chem. Soc.* 121, 2146-61 (1922).—Fructose gives 2 cryst. diacetone compds. (α - and β -) which are convertible into isomeric monoacetones. The two α -derivs. are based on the stable type of fructose. Fructosemonoacetone, prepd. from the diacetone compd. ($[\alpha]_D -123^\circ$) had a value of $[\alpha]_D^{20} -145^\circ$ instead of -158.9°. MeI and Ag₂O, the application of which was repeated 6 times, converted this into trimethylfructosemonoacetone, $b_D 135-8^\circ$, $n_D 1.4575$, $[\alpha]_D^{20}$ in H₂O, -147.9° for c 0.902; in EtOH, -125.7° for c 0.887; in AcMe, -125.0 for c 1.208. By means of hydrolysis, condensation with MeOH, methylation with Ag₂O and MeI and final hydrolysis, this deriv. was converted into tetramethylfructose, identical with a known sample which possesses the butylene-oxide linkage. These results establish the constitution of the mono- and diacetone compds. as I and II. Supplementary evidence will be furnished by the prepn. of the trimethylfructosemonoacetone of the γ -series. d - γ -Methylfructoside, when subjected to the action of acidified AcMe, loses its Me group and forms fructosediacetone:



this product consists of the l - α -form, showing that complete rearrangement of the O linkage had taken place during the reaction. In considering the structure of glucose-acetones, the diacetone was converted into the monoacetone, this transformed into trimethylglucosemonoacetone and the product hydrolyzed to trimethyl- γ -glucose, with $[\alpha]_D -37.3^\circ$. The tentative structure III is offered as best expressing the properties and formation of the glucose acetones. The behavior of alk. KMnO₄ on various derivs. of C₃H₅(OH)₂ is reported as indicating that Karrer chose a particularly uncertain re-

agent for application to derivs. of sugars. Glycerolacetone, when perfectly pure, is stable to neutral KMnO_4 , but reduces alk. KMnO_4 . The same is true of the Me deriv.



C. J. WEST

The sulfuric esters of sugars. HEINZ OHLE. *Biochem. Z.* 131, 601-11(1922).—To 11 g. glucose in 50 cc. pyridine, 3.4 cc. ClHSO_3 in 10 cc. EtOH-free CHCl_3 is added. After standing overnight at room temp. the solvents are evapd., 10 g. NaOAc in 30 cc. boiling Ac_2O and 20 cc. HOAc are added to the residue, and the ppt. is filtered after 2 hrs., standing at 60-70°. This is refiltered after chilling and pentaacetylglucose extd. with ether. The ppt. is dissolved in 50 cc. H_2O , extd. with ether, and the aq. soln. evapd. and the residue dissolved in 100 cc. abs. EtOH. On spontaneous evapn. and the addn. of 1% H_2O , 5 g. tetraacetylglucose 6-sulfate (A) crystd.; it m. 137° (decompn.), $[\alpha]_D^{19}$ 12.45° (H_2O). Decompn. of 10 g. of the Na salt with pyridine-HCl in pyridine yielded 8.3 g. pyridine salt (B), $[\alpha]_D^{20}$ 12.61°. Crystd. from EtOH (5 parts) it m. 158-160°. Hydrolysis (by 24-36 hrs. contact) with Ba(OH)_2 is accompanied by some splitting off of H_2SO_4 . After removal of the Ba, the calcd. amt. of brucine is added, and the residue after concn. extd. with EtOH. There remains undissolved *brucineglucose 6-sulfate*, slender plates from H_2O , m. (decompn.) 183°, $[\alpha]_D^{17}$ 4.07°. After 12 hrs. $[\alpha]_D^{17}$ -0.28°. 4 g. pyridinetetraacetylglucose 1-sulfate (C) formed by the action of 1.4 cc. ClHSO_3 in 10 cc. CHCl_3 on 8 g. tetraacetylglucose, crystals from EtOH, m. 127°, $[\alpha]_D^{17.5}$ -4.65° (H_2O), easily decompd. by hot EtOH, and H_2O , or dry heat. The sodium salt may be prepd. by the action of NaOAc in hot EtOH on C, m. 149-151°, $[\alpha]_D^{17}$ -6.23° (H_2O), unstable on heating. An addition product (analyzing C 47.17%, H 5.51%, S 3.53 %), is formed on shaking 8.4 g. acetobromoglucose in 50 cc. pyridine with 3.2 g. Ag_2SO_4 for 15 hrs., fine needles, recrystd. from EtOH, m. 141-2°. After long boiling with MeOH it m. 143-4°. 3 g. of an identical substance was formed by boiling 8.4 g. acetobromoglucose in 100 cc. dry Me_2CO with 7 g. Ag_2SO_4 and 10 cc. pyridine. Recrystd. from EtOH, it m. 153-4°, $[\alpha]_D^{15.5}$ -12.87° (in CHCl_3). Heated *in vacuo* at 100° it loses 1.4% in wt., m. 147-9°, is sol. in Me_2CO , CHCl_3 , MeOH, HOAc and EtOH, insol. in petroleum ether, and C_6H_6 , slightly sol. in cold EtOH and H_2O . The H_2SO_4 is freed on long boiling in neutral soln. or instantaneously on treatment with Ba(OH)_2 . This substance (m. 143-4°) (1.4 g.) is also obtained by the action of 0.28 g. Ag_2CO_3 on 1 g. C and 0.8 g. acetobromoglucose. Sodium salt of triacetyl- β -methylglucoside sulfate (D) (20% yield), prepd. as A, prisms from EtOH, contg. 1.5 mols. H_2O , m. 141-2° (decompn.), $[\alpha]_D^{18}$ -5.24° (in H_2O), sol. in EtOH, CHCl_3 and C_6H_6 , insol. in AmOH; the SO_3H group is stable. Pyridine salt (sol. in H_2O , EtOH and CHCl_3 , insol. in gasoline), decomp. on warming. 0.5 g. β -methylglucoside sulfate, prepd. from 1.0 g. D as the brucine salt, crystals from a mixture of EtOH and Me_2CO contg. 1 mol. EtOH, m. gradually 136-55° (decompn.), $[\alpha]_D^{19.5}$ -32.54°.

I. P. ROLF

The constitution of vaccinin. HEINZ OHLE. *Biochem. Z.* 131, 611-3(1922).—Although by its derivation from diacetoneglucose, vaccinin has been considered a β -benzoylglucose, recent studies on glucose sulfuric acids (cf. preceding abstr.) indicate

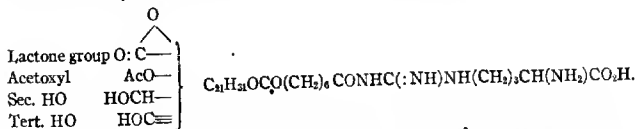
that it is *6-benzoylglucose*. Benzoylation of monoacetoneglucose yields a substance identical with that obtained by hydrolysis of diacetonebenzoylglucose. By treating 11 g. monoacetoneglucose in 50 cc. pyridine with 5.75 cc. BzCl in 15 cc. CHCl_3 without cooling, 8.8 g. *6-benzoylmonoacetoneglucose* (A) crystals, on the addn. of H_2O to the concd. residue. Crystd. from EtOH , *m.* 194-6°, $[\alpha]_D^{20}$ 7.97°. By the use of 2 g. anhyd. CuSO_4 as catalyst, 1.7 g. diacetoneglucose (recrystd., *m.* 105°) may be obtained from 2 g. monoacetoneglucose (by shaking for 36 hrs. in dry acetone and pptg. the concd. residue with benzene). A second acetone group cannot, however, be introduced into A by the neutral catalyst. That the Bz group in the latter occupies position 6, and that CuSO_4 is unable to effect a rearrangement, is postulated by O., who hopes by the use of a low H^+ concn. to isolate the intermediate 3-benzoylmonoacetoneglucose formed in the decompn. of benzoyldiacetoneglucose.

I. P. ROSE

Alkaline copper oxide solutions and copper oxide-amine-cellulose solutions.
 II. WILHELM TRAUBE. *Ber.* 55B, 1899-912 (1922); cf. *C. A.* 16, 1934.—It was shown in the 1st paper that aq. cupriethylenediamine hydroxide (A), $[\text{CuEn}_2][\text{OH}]_2$, prepd. by dissolving the calcd. amt. of $\text{Cu}(\text{OH})_2$ in aq. $(\text{CH}_2\text{NH}_2)_2$ (B), forms with poly-HO compds. (glycerol, mannitol, etc.) alcoholates whose solns. can dissolve more $\text{Cu}(\text{OH})_2$. For glycerol the reactions were represented by the equations $2\text{C}_2\text{H}_5\text{OCH}_2\text{OH} + \text{A} \rightleftharpoons [\text{CuEn}_2](\text{OCH}_2\text{C}_2\text{H}_5\text{O})_2$ (C) + $2\text{H}_2\text{O}$ (1), and $\text{C} + \text{Cu}(\text{OH})_2 = [\text{CuEn}_2](\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O})_2\text{Cu}$ (D) + $2\text{H}_2\text{O}$ (2). At that time the formation of D directly according to the equation $2\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{OH} + 2\text{A} = \text{D} + 4\text{H}_2\text{O} + 2\text{B}$ (3) was not discussed. Further study has shown that as a matter of fact the reaction proceeds to a considerable extent according to (3), i. e., with regeneration of free B. An equimol. soln. of glycerol and A behaves like a soln. contg. free B; it can dissolve not only $\text{Cu}(\text{OH})_2$, which could be explained by (2), but also other metallic hydroxides or oxides, such as Ag_2O ; aq. glycerol alone dissolves no Ag_2O and aq. A (18% soln.) dissolves only 0.16% Ag after shaking 30 min. with moist Ag_2O , but if previously treated with about 1 mol. glycerol it dissolves 1.7%. Since the resulting Ag base has the compn. $[\text{AgEn}_2]\text{OH}$ it is possible to calc. how much free B there must have been present in the soln. of A and glycerol; under the above conditions of concn., this amts. to about 25%. The cupriethylenediamine cupric glycerate (D) can be isolated by concg. an 18% soln. of A and about 2 mols. glycerol *in vacuo* over H_2SO_4 , spreading on clay and drying over CaCl_2 ; it forms a light blue-violet powder with $4\text{H}_2\text{O}$ (C:N:Cu ratios found on 3 samples 10:3.6:2.2, 10:3.7:2.3 and 10:3.9:2.3, resp.), becomes greenish after a few days, dissolves clear in H_2O , when fresh, with dark blue-violet color but soon begins to deposit $\text{Cu}(\text{OH})_2$. The reactions between copper-amines and more complex poly-HO compds., such as cellulose, are undoubtedly analogous. Of all the metals (Ag, Co, Ni, Zn, Cd) which can form complex cations with NH_3 and its substitution products, Cu alone has the additional property of being dissolved as the hydroxide in the presence of strong bases by poly-HO compds. When, therefore, the bases derived from these other metallic hydroxides react with poly-HO compds., they undoubtedly form alcoholates analogous to C but the reaction stops at that point; this is probably why the Cu bases alone dissolve cellulose. The process whereby glycerol prevents the pptn. of $\text{Co}(\text{OH})_2$ by alkalis from solns. of Co salts is not the same as in the case of Cu salts; the former solns. do not contain the CoO as a glycerate but as a colloid which can be completely flocculated by shaking with BaSO_4 . If all the Co in a 9% soln. of the cryst. sulfate is pptd. with about 6 mols. of 9% NaOH and 2-3 mols. glycerol are immediately added not a trace of the $\text{Co}(\text{OH})_2$ dissolves, while under the same conditions $\text{Cu}(\text{OH})_2$ dissolves completely and quickly. The above results are completely confirmed by the behavior of the same Cu bases with biuret (E). When 2 mols. E is treated with 1 mol. A, the resulting violet-red liquid can dissolve considerably more $\text{Cu}(\text{OH})_2$ and on addn. of alc. there seps. the

compound $[\text{CuE}_2\text{N}_2](\text{C}_4\text{O}_3\text{N}_3\text{H}_5)_2\text{Cu}$, flat red-violet needles with 1 H_2O from H_2O - EtOH , sol. in H_2O with KMnO_4 -color, also seps. from 3 parts H_2O on concn. *in vacuo* over H_2SO_4 in rhombic violet-blue tables with $7\text{H}_2\text{O}$. The characteristic red-violet color shows beyond doubt that one Cu atom of the compd. is combined in the same way as in Schiff's Cu K biuret, *i. e.*, that it has directly replaced 1 of the H atoms of E, while the other Cu atom forms part of the complex $[\text{CuE}_2\text{N}_2]$. The K in Schiff's salt can be replaced by other compd. bases than $[\text{CuE}_2\text{N}_2]$, *i. e.*, the biuret reaction can be carried out with strong org. bases instead of alkalis. Thus, 10% aq. Et_4NOH does not of itself dissolve $\text{Cu}(\text{OH})_2$, but on addn. of E there results a fine red soln.; aq. guanidine behaves similarly. In all of these reactions the E can be replaced by any of the substances which give the so-called biuret test. As reported in the first paper, the amt. of NH_4OH necessary to dissolve a given amt. of $\text{Cu}(\text{OH})_2$ decreases as increasing amts. of glycerol are added; thus, 20% NH_4OH dissolves only 1 mol. $\text{Cu}(\text{OH})_2$ to 55 mols. NH_3 , but if 0.5 mol. glycerol per mol. NH_3 is used, the Cu: NH_3 ratio in the resulting soln. is 1:2.49; similarly 22.2% MeNH_2 alone dissolves only 0.526% Cu and in the presence of 0.5 mol. glycerol 9.32%; Me_2NH alone dissolves practically no $\text{Cu}(\text{OH})_2$ and with glycerol 1 atom Cu to 14.47 mols. Me_2NH . E similarly increases the soly. of Cu in NH_4OH and amines. The *cupriethylenediamine cupric biuret*, $[\text{Cu}(\text{NH}_2)_2][(\text{C}_4\text{O}_3\text{N}_3\text{H}_5)_2\text{Cu}]$, can be isolated in red-violet prisms with $3\text{H}_2\text{O}$. C. A. R.

The poisonous substance of toads. HEINRICH WIELAND AND RICHARD ALLES. *Ber.* 55B, 1789-98(1922); cf. C. A. 16, 3073.—In working up again several thousand toad skins to obtain a new supply of bufotalin (A), $\text{C}_{28}\text{H}_{48}\text{O}_6$, special precautions were taken in the hope of increasing the yield of A; the alc. ext. this time was cvapd. *in vacuo* to complete dryness, at a low temp. but the yield of A, instead of being increased, was only a few% of that formerly obtained. A careful investigation of the less promising fractions of the material revealed the reason for this; there was isolated a much more complex substance than A, *viz.* bufoloxin (B), $\text{C}_{40}\text{H}_{72}\text{O}_{11}\text{N}_4$ (later also isolated from the secretion squeezed out of the ear glands of the living toads; cf. Handovsky, C. A. 14, 2663) whose color reaction with concd. H_2SO_4 and Ac_2O at once betrayed its close connection with A. It was therefore concluded that B is the original toad venom and that the A was produced as a kind of "genin" from the B in the treatment of the skin exts. in the earlier work. On boiling with very dil HCl, the nucleus of the mol. is split off from the B as bufotalien (C), $\text{C}_{28}\text{H}_{48}\text{O}_4$; at the same time there is produced, besides H_2O and AcOH , *suberylarginine* (D), smoothly decompd. by concd. HCl into suberic acid (E) and arginine. Since B has hardly any acid properties it can be concluded with certainty that in the B the D is united to A in ester-like combination through the CO_2H group of the E residue; the earlier work indicates that it is this union which is the most easily ruptured, the splitting off of the D probably resulting in the production of the 2nd double bond in A (B, like cholesterol, contains only 1 double bond). The facts thus far known can be represented by the following formula for B:



Like A itself, acetylbufotalin slowly stirred into concd. HCl loses 1 mol. each of AcOH and H_2O , giving acetylbufotalien, $\text{C}_{28}\text{H}_{48}\text{O}_4$, light yellow needles with faint greenish tinge from alc., m. 184° , identical with the product obtained by acetylation of bufotalien; with Pd, black in Et_2O , it takes up 8 atoms of O, yielding *acetylbufotalan*, $\text{C}_{28}\text{H}_{48}\text{O}_6$, needles from alc., m. 165° . The B was found in the Et_2O - and especially the CHCl_3 -

insol. residues which are obtained in the process earlier described for the isolation of A: 110 g. of such a CHCl_3 -insol. residue was digested at $40-50^\circ$ with 300 cc. alc. until the insol. portion had become powdery, filtered, washed with alc. until the washings no longer gave the color reaction of A, concd. to a sirup at 40° , vigorously kneaded with several 1-l. portions of H_2O , allowed to stand 24 hrs., filtered and dried; the amorphous product (36 g.) was dissolved in just the necessary amt. of hot alc., cooled, freed from most of the dark tar by slowly adding petr. ether until the soln. assumed a reddish yellow tinge, filtered, treated with H_2O with vigorous stirring, until a turbidity was produced, sepd. from the petr. ether layer and allowed to stand 15 hrs., whereupon the B sepd. in cryst. form on the walls of the vessel; after repeated crystn. from 96% alc. it was obtained in druses of fine needles, m. $204-5^\circ$ (violent decompn.), practically insol. in H_2O , gives the same color reaction as A with Ac_2O and H_2SO_4 , is insol. in dil. mineral acids and in 1 equiv. of alkali and dissolves rapidly in an excess of alkali only when in finely divided form, as obtained by pptn. from alc. with H_2O ; alc. KOH opens the lactone ring and produces an acid at once sol. in alkalies; phosphotungstic acid ppts. it from dil. alc. soln.; boiling in alc. for 80 hrs. leaves it unchanged; with H and Pd black in 80% alc. it yields *hydrobifoloxin*, $\text{C}_{20}\text{H}_{30}\text{O}_4\text{N}_4$, fine needles from alc., m. 187° , no longer gives the color reaction of B. The decompn. of B into C and D is smoothly effected by boiling 0.5 g. B 4-5 hrs. with 5 cc. alc. and 5 cc. of 2 N HCl. The D could not be obtained in cryst. form; it is easily sol. in H_2O , completely pptd. by phosphotungstic acid and reddens litmus.

C. A. R.

The phytosterols of ragweed pollen. F. W. HEYL. *J. Am. Chem. Soc.* **44**, 2283-6 (1922).—In the unsaponifiable fraction of pollen fat from ragweed (*Ambrosia artemisiifolia* L.) have been identified traces of a hydrocarbon, along with appreciable amts. of the higher homologs of the paraffin alc. series; the presence of cetyl and octadecyl alcs. has been established. The phytosterol fraction (0.55% of the pollen) is an optically active complex cryst. mixt. which resists to a remarkable degree all efforts at sepn. by the regular methods of fractional crystn. By persistent recrystn. of the acetates from Ac_2O , however, one of the components of the mixt. has been satisfactorily characterized. This *ambrosterol*, $\text{C}_{28}\text{H}_{48}\text{O}$, needles with 1 H_2O from 95% alc., m. $147-9^\circ$, gives a fairly persistent deep violet or blue color when a trace is hoiled with 10 drops Ac_2O , cooled, dild. with 10 cc. CHCl_3 and treated with a drop of concd. H_2SO_4 ; acetate, plates, m. $112-3^\circ$, $[\alpha]_D^{27.7}$ (CHCl_3). The phytosterol fraction also yields a compound $\text{C}_{27}\text{H}_{46}\text{O}$, needles with $1\frac{1}{2}\text{H}_2\text{O}$ from alc., m. $147.5-8.0^\circ$, and there is much evidence of the presence in considerable amts. of a more highly oxygenated substance, perhaps a hydroxyphytosterol, $\text{C}_{27}\text{H}_{46}\text{O}_2$.

C. A. R.

Side-chain oxidations with potassium permanganate. II. L. A. BIGELOW. *J. Am. Chem. Soc.* **44**, 2010-9 (1922); cf. C. A. **13**, 2667.—This is an extension to the bromotoluenes of the study of the nitrotoluenes reported in the 1st paper. The oxidations were carried out in alk. or neutral media on a moderately large lab. scale, a product of high com. quality and a max. yield being the aim rather than one of greater purity, with decreased yield. Nearly all the influences which have been brought to bear upon the oxidations have been found to have a considerable effect upon the reactions, but the results in every case have been merely to alter the proportion of PhBr attacked by the KMnO_4 , emphasizing the conclusion drawn on the earlier paper, viz., that the quantity of org. matter entirely destroyed during the reaction is practically independent of variations of procedure and that 2 entirely independent changes occur within the reacting mixt.: the oxidation of the side-chain to CO_2H , and the decompn. of the KMnO_4 into Mn oxides and free O; differing conditions merely accelerate the one or the other of these changes, causing various amts. of material to be attacked before all of the KMnO_4 has been destroyed. Detailed descriptions of the conditions found

to give the best yields of the 3 bromotoluenes are given. *o*-BrC₆H₄Me, b. 181–2°, was obtained in 40% yield from com. *o*-MeC₆H₄NH₂ diazotized in HBr (d. 1.49) at 10° and heated on the H₂O bath with Cu powder. The *m*-compd., b. 183–4°, is obtained in 36% yield by refluxing com. *p*-MeC₆H₄NH₂ in glacial AcOH, brominating below 50° with Br in AcOH, pouring into H₂O, treating the resulting dried 3,4-Br(AcNH)C₆H₂Me in 95% alc. with solid NaOH, pouring into H₂O, diazotizing the Br(H₂N)C₆H₂Me in alc. H₂SO₄ and heating with Cu powder. The *p*-compd., m. 26°, b. 184–5°, is obtained in 70% yield from *p*-MeC₆H₄NH₂ by the Sandmeyer reaction. The essential results of the oxidation expts. are as follows: A gradually increasing concn. of alkali in the reaction mixt. is on the whole unfavorable to the oxidation of all the bromotoluenes but slightly alk. soln. is more favorable than an entirely neutral medium; increasing diln. of the soln. is favorable to the oxidation, as is an excess of the KMnO₄ above the calcd. amt.; while the rates of oxidation of the 3 compds. are essentially the same the *p*-compd. gives the highest yield of BrC₆H₄CO₂H, the *m*-compd. is next and the *o*-isomer gives the lowest yield. The essential point of difference between these results and those obtained with the nitrotoluenes is the fact that with the latter the presence of alkali was very favorable to the oxidation of the *o*- and *p*-compds. C. A. R.

Trifluoromethylcyclohexanone. FRÉD. SWARTS. *Bull. acad. roy. Belgique, extraits des Bull. Classe des Sci.* June 1922, 331–43 pp.—Trifluoromethylcyclohexanone (A) has already been reported (C. A. 16, 2316). The solidification point, in conjunction with Timmermans, was found to be –103.4° and –103.5°. Trifluorotoluene warmed at 180° with fuming HBr is quant. transformed into BzOH in 48 hrs. 6 g. A were heated at 180° for 80 hrs. with HBr (d. 1.783) and SiO₂ was added to combine with HF. The reaction product was treated with Et₂O, and then the ext. was treated with H₂O. Hexahydrobenzoic acid equiv. to a hydrolysis of 3% was found. A in alc. is not attacked by soda nor by Hg-Na. A is attacked by Br in the cold very slowly and also at the b. p. In closed tubes the reaction required 17 days at 108° for completion. The mono-Br deriv. is brominated more readily than A and unchanged A is always present. Monobromotrifluoromethylcyclohexane (B), b. 177–8°, is a colorless liquid, stable in the light, has a penetrating odor, is fluid at –70°, *d*₄ 1.561. Dibromotrifluoromethylcyclohexane (C), b. 218–20° (slight decompn.), is fluid at –80°, *d*₄ 1.912. Tribromotrifluoromethylcyclohexane h. 260–5° (decompn.). 7.5 g. A were heated during 13 days at 170° with 64 g. Br. Free Br remained after that time. Br was removed with NaHSO₃ and the mixt. was then shaken with NaOH soln. When H₂SO₄ was added 3,4- and also 2,5-Br₂C₆H₃CO₂H were pptd. A third product, b. near 310°, was not identified. The action of Br is similar to that found by Bodroux and Taboury (C. A. 5, 3232) in the case of methylcyclohexane in the presence of AlBr₃. They obtained pentabromotoluene, whereas the CO₂H group causes substitution of only 2 of the 5 H atoms of the ring. When A was refluxed 20 hrs. with 5% KMnO₄ and the reaction mixt. was steam-distd. the oil which passed over was treated with HNO₃ (d. 1.5). The absence of a NO₂ deriv. showed that trifluorotoluene had not been formed. KMnO₄ interacted according to the equation: A + 18O = 7CO₂ + 3H₂ + 4H₂O. When B was warmed 36 hrs. with H₂O and HgO, HgBr₂ sepd. out. Trifluoromethylcyclohexane (D), b. 104.5–5.5°, was obtained, mobile liquid having the odor of the hydrocarbons of this group, *d*₄ 1.127. The compd. was detd. with a standard Br soln. and the bromo derivative b. 219–20°. C when reduced with Zn in alc. gave D or the isomer; the quantity produced was too small for confirmation but the m. ps. were identical. The quant. transformation of C into D shows that the 2 Br atoms are vicinal and in the *syn*-position. One ought to be in the 3-position relative to the CF₃-group but S. has not detd. whether the other is in the 4- or the 2-position. A when nitrated with HNO₃ (d. 1.5) at 130° during 24–8 hrs. was destructively oxidized. Nitrotrifluoromethylcyclohexane (E),

viscous liquid, with a pronounced odor, $d_{40} 1.3154$, $b_{20} 124.5^\circ$, sol. in aq. alkalis, and its Na deriv. is very sol. in alc. A when treated with dil. HNO_3 was oxidized and certain Ba salts of the oxidation products were obtained, among them $(\text{CH}_3\text{CO}_2)_2\text{Ba}$. The small amt. of CO_2 formed as well as the relatively small amt. of $(\text{CH}_3\text{CO}_2\text{H})_2$ pointed to the formation of a volatile F acid; consequently in the distillate was found $\text{CF}_3\text{CO}_2\text{H}$. The ester and the amide were prepd. $\text{CF}_3\text{CO}_2\text{H}$ and trifluoromethyladipic acid were prepd. by treating 16 g. E with 40 cc. dil. HNO_3 (d. 1.15) at 135° . The tubes were opened after 48 and 96 hrs., when most of E had disappeared. The soln. was distd. and 7.82 g. Ba- $(\text{CF}_3\text{CO}_2)_2$ were obtained. The nonvolatile residue when extd. with Et_2O gave 5.39 g. acid.

H. E. W.

Preparation of phenylglycine-*o*-carboxylic acid. HERBERT L. HALLER. *J. Ind. Eng. Chem.* 14, 1040-4(1922).—Two general methods for prep. phenylglycine-*o*-carboxylic acid (A) are the condensation of $\text{C}_6\text{H}_5(\text{NH}_2)\text{CO}_2\text{H}$ (B) with $\text{CHCl}_3\text{CO}_2\text{H}$ (C); and the treatment of B with CH_2O and KCN. A study of the second method will be reported later. The relative cost of prep. A by the two methods is not known. A review of the literature is given in the article. Expts. were carried out in which the concn. of the reagents was the only variable, the time of reaction, ratio of B to C and the temp. being held const. The time of reaction was then made the only variable in a series of tests. Data on all of the factors affecting the yield of A were secured. The max. yield was obtained when the time of reaction was 1 hr. and the concn. is 25 g. B and 17.2 g. C in 200 cc. H_2O . At a higher concn. the reaction between B and C takes place more rapidly but more of B is destroyed. When an alk. carbonate is the condensing agent, a better yield of A results than when an equiv. amt. of an alkali hydroxide is used, probably the result of the much less rapid hydrolysis of C by carbonates. The max. yield of A is obtained when the reaction is conducted at 90° for 1 hr. Approx. identical results were obtained at 70° for 4 hrs. Below this temp. the reaction proceeds too slowly.

H. E. W.

Nitro derivatives of *m*-nitrodimethylaniline. AQUILA FORSTER AND WM. COULSON. *J. Chem. Soc.* 121, 1988-97(1922).—This is a running account of the orientation of certain NO_2 derivs. obtained during the study of $3\text{-O}_2\text{NC}_6\text{H}_4\text{NHMe}$ (A) and $3\text{-O}_2\text{NC}_6\text{H}_4\text{NMe}_2$ (B). It is believed that the following are new compds., but no description or properties, beside of the m. p. are given. B, with 70% HNO_3 , gives 2,3,6-trinitrodimethylaniline, m. 138° . Of the 2 $(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{NMe}_2$, the one m. 112° is the 3,6-derivative while the one m. 176° is the 3,4-derivative. 2,3,6- $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{NMe}_2$, treated with 1 mol. HNO_3 , gives 2,3,4,6-tetranitrodimethylaniline, m. 153° . 3,4,6- $(\text{O}_2\text{N})_3\text{C}_6\text{H}_3\text{NMe}_2$, on further nitration, gives 3,4,6-trinitrophenylmethylnitroamine (C), needles m. 143.5° . H_2SO_4 transforms this into 2,3,4,6-tetranitromonomethylaniline, m. 127° . Boiling 90% HNO_3 slowly converts C to the tetranitro derivative, m. 174° . NH_4OH gave 4,6-dinitro-3-aminophenylmethylnitroamine, m. 169° . One mol. KOH in boiling alc. converted it into the 3-ethoxy derivative, m. 135.5° , which with alc. MeNH_2 gave 4,6-dinitro-3-methylaminophenylmethylnitroamine, m. 181.5° ; nitrating in boiling 90% HNO_3 gave 2,4,6-trinitro-1,3-di[methylnitroamino]benzene, m. 206° . 2,3,4-Trinitrophenylmethylnitroamine, m. 122.5° . The positions occupied by the NO_2 groups during the nitrations appear to be largely controlled by steric hindrance. This is discussed. 4-Bromo-2,3,6-trinitrodimethylaniline, scarlet, m. 167° ; on further nitration this yields 4-bromo-2,3,6-trinitrophenylmethylnitroamine, m. 165° . 4-Bromo-3,6-dinitrodimethylaniline; scarlet form, m. 108° ; orange form, m. 174° ; 6-bromo-3,4-dinitrodimethylaniline; scarlet form, m. 119° orange form, m. 131° . 6-Bromo-2,3,4-trinitrophenylmethylnitroamine, m. 116° . 4-Bromo-2,6-dinitro-3-methylaminodimethylaniline, m. 114° . The 3- NO_2 group of 3,4- $(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{NMe}_2$ is mobile and with MeNH_2 gives the 3-methylamino derivative, m. 117° . In the 2,3,6- $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{NMe}_2$, the 3- NO_2 group was transformed into

the 3-hydroxyl derivative, m. 191°, the 3-amino derivative, m. 160°, the 3-methylamino derivative, m. 121°, and the 3-anilino derivative, m. 135°. In 2,3,4,6-(O₂N)₂C₆HNMes, the 3-NO₂ group was replaced by 3-amino group, m. 187°. Several examples of chromoisomerism are recorded.

C. J. WEST

The dinitro derivatives of *p*-dichlorobenzene. A. L. MACLEOD, M. C. PFUND AND M. L. KILPATRICK. *J. Am. Chem. Soc.* 44, 2260-71(1922).—When Nason took up the study of these compds. (*C. A.* 12, 2551), 2 of the 3 theoretically possible dinitro-1,4-dichlorobenzenes were known: the 2,6-compd. (A), m. 104-6°, and the 2,3-deriv. (B), m. 101°. By careful crystn. from alc. of the products of nitration of *p*-C₆H₄Cl₂ N. succeeded in isolating a compd. (C), m. 81°, of the same empirical compn. as the above 2 substances, and as on reduction this gave 1,4,2,5-C₆H₂(NH₂)₂Cl₂ (although only in 35% yield) it was concluded that C is 1,4,2,5-C₆H₂Cl₂(NO₂)₂ (D). A study of the action of alc. NH₃ on the 3 compds. showed, however, that the main product obtained from C is identical with that obtained from A. In the meantime, Holliman, Hollander and van Haefen (*C. A.* 15, 3631), taking advantage of the fact that the different dinitro-*p*-dichlorobenzenes react with alc. NH₃ at different rates, succeeded in isolating the true D, m. 119°. They also evidently obtained C but failed to purify it; they state that after sepg. A and B they obtained a white mass of cauliflower-like crystals with indefinite m. p., which could not be sepd. into its components by crystn. M., P. and K., however, have without difficulty obtained a product melting within 0.5° whose m. p. remains unchanged after 5-6 crystns. from alc. or after as many crystns. from half a dozen different solvents in succession, which can be sublimed or distd. unchanged, b_p 198°, mol. wt. in freezing C₆H₄ 226-8. In its reactions with alc. NH₃, with PhNH₂, with Na alcoholates and on reduction, it invariably forms both *m*- and *p*-dinitro derivs. (Nason obtained no trace of a *m*-diamine on reduction, but this was apparently due to the method of extn. used.) A study of the f. p. curves has shown that C is a mol. compd. of probably 2 mols. D with 3 of A; in soln., it exists only in the dissociated state. The crude nitration product of *p*-C₆H₄Cl₂ (100 g.) in 3 l. of 95% alc. when cooled in ice deposits A in comparatively pure form. If 600-50 cc. per l. of the mother liquor is distd. off in winter or 700-50 cc. in summer and the residue is cooled very gradually in the H₂O bath overnight, the C seps. out in fairly pure form. If, now, 25 g. of the C is allowed to stand 24 hrs. or more at room temp. with 175 cc. of 4 N alc. NH₃, the A component of the C is entirely transformed into 4,2,6-Cl(O₂N)₂C₆H₂NH₂ while the D remains for the most part unchanged and can be obtained from CHCl₃ in lemon-yellow crystals m. 117.5°. A b. 302°, C 302.5°, D 304°. With alc. NH₃ A reacts readily, even at room temp., giving exclusively 4,2,6-Cl(O₂N)₂C₆H₂NH₂, m. 145°. B yields chiefly 3,6,2-Cl₂(O₂N)₂C₆H₂NH₂, m. 67°, together with a little (8-9%) 2,3-dinitro-1,4-diaminobenzene, mustard-yellow microneedles, m. 241-50° (decompn.). D yields chiefly 3,6,4-Cl₂(O₂N)₂C₆H₂NH₂, m. 153°, and 27% 2,5-dinitro-*p*-phenylenediamine, reddish brown needles from alc., m. 295-300° (decompn.). C gives 4,2,6-Cl(O₂N)₂C₆H₂NH₂, 2,5,4-Cl₂(O₂N)₂C₆H₂NH₂ and 1,4,2,5-C₆H₂(NH₂)₂(NO₂)₂. With SnCl₂ and Sn in concd. HCl C yields 1,4,2,5- and 1,4,2,6-C₆H₂Cl₂(NH₂)₂, m. 164° and 105.5°, resp. 1,4-Dichloro-2,3-diaminobenzene, from B, silky needles from 50% alc., m. 98°, condenses with benzil in alc. on the H₂O bath to 1,4-dichlorodiphenylguinoxaline, needles from C₆H₅-EtOH, m. 214°.

C. A. R.

The interaction of aniline and acraldehyde. F. G. MANN. *J. Chem. Soc.* 121, 2178-82(1922).—The base C₁₄H₁₀ON₂ is formed by the interaction of CH₂:CHCHO and PhNH₂ in a freezing mixt., amorphous, m. 84°. Chloroplatinate, pale buff-colored powder, decomp. below 300°. Picrate, greenish brown, amorphous compd. m. 120-1° (decompn.). Bromide, C₁₄H₁₀ON₂Br, pale brown, hygroscopic powder, m. 178-80° (decompn.). The base, fused or exposed in soln., develops a deep red color owing to

oxidation to the compound $C_{30}H_{33}O_8N_4$, brick-red powder, m. 143° (decompn.). *Chloroplatinate*, dark red powder, m. 280° (decompn.). *Picrate* dark, greenish brown powder, m. 140° (decompn.). *Bromide*, dark reddish brown powder, m. 280° (decompn.). The only product obtained upon dry distn., or distn. with metallic oxides or $PhNO_2$ was $PhNH_2$. p - $MeC_6H_4NH_2$ and $CH_3:CHCHO$ give a compound $C_{20}H_{24}ON_2$, cream-colored amorphous ppt., m. 111° ; on distn. this gives H_2O and p - $MeC_6H_4NH_2$.

C. J. WEST

Condensation of aromatic *o*-aminosulfonic acids with isocyanic acid. J. R. SCORR AND J. B. COHEN. *J. Chem. Soc.* 121, 2034-51 (1922).—The attempt to prep. anhydrides (hydantoin) from *o*-carbamidosulfonic acids was unsuccessful. In *p*-substituted derivs., when $X = NO_2$, $HCNO$ does not condense with the NH_2 group; when $X = H, Me$ or SO_3H , 1 mol. $HCNO$ condenses with 1 mol. of acid, giving a carbamido acid. When $X = Cl, Br$, or I , 2 mols. $HCNO$ condense with 1 of the acid, giving a deriv. of *asymphenylbiuret*, $2,4-HO_2S(O_2N)C_6H_4NH_2$: *Potassium salt*, anhydrous, orange, rhombic plates, sparingly sol. in H_2O . *Ammonium salt*, small, orange rhombohedral, sparingly sol. in cold H_2O , chars 290° . *Aniline salt*, yellow, rhombic plates, decomp. $236-7^\circ$. The only action of $KCNO$ was to ppt. the K salt. $3,4-HO_2S(H_2N)C_6H_3Me$ (A): *Ammonium salt*, small prisms, m. $241-3^\circ$ (decompn.); *aniline salt*, needles, m. $237-41^\circ$ (decompn.). A mixt. of the acid and $KCNO$, treated with HCl , gave *p*-carbamidotoluene-*m*-sulfonic acid (B), small, rectangular plates or prisms, decomp. $22-3^\circ$. Boiling Ac_2O regenerates A. *Potassium salt* (C), with 1 H_2O of crystn., small prisms. *Ammonium salt*, small prisms, decomp. 258° . *Aniline salt*, needles or prisms, m. $170-1^\circ$, then $247-9^\circ$. *Acetate*, microneedles, decomp. $291-3^\circ$, contg. 1 H_2O of crystn. The free acid could not be obtained because of hydrolysis of the Ac group. $POCl_3$ and B give A and a small amt. of a compound, $C_8H_5O_2N_3S \cdot 2H_2O$, thin rhombic plates, m. 272.5° , which may be an anhydride. $PhNH_2$ and B give $(PhNH)_2CO$ and *ammonium sym-di-p-tolylcarbamide-2,2-disulfonate*, small pale yellow plates, decomp. $275-6^\circ$, analyzed as the *potassium salt*, microneedles or plates. *o*- $H_2NC_6H_4SO_3H$: *Aniline salt*, needles or prisms, m. $180-210^\circ$ (decompn.). *o*-Carbamidobenzenesulfonic acid, rhombic or hexagonal plates, decomp. $215-30^\circ$. *Potassium salt*, hexagonal plates with 1 H_2O . *Ammonium salt*, small prisms, decomp. 237° . *Aniline salt*, needles, m. $159-61^\circ$ (decompn.). *Acetate of potassium salt*, needles with 1 H_2O , did not m. 310° . *Potassium phenylcarbamide-2,4-disulfonate*, white powder contg. 1 H_2O , very sol. in H_2O . $2,4-(HO_2S)BrC_6H_3NH_2$ (D): *Sodium salt*, small pink, elongated plates. *Ammonium salt*, small plates, m. $226-7^\circ$, very sol. in H_2O . *Aniline salt*, small, glistening rhombic plates, m. 214° . Condensation with 2 mols. $HCNO$ gave *potassium p-bromophenylbiuret-o-sulfonate* (E), faintly yellow needles, decomp. 210° . It contains $2H_2O$ of crystn. When D is purified according to Kreis (*Ann.* 286, 381), the condensation product forms large silky yellow needles, m. 181° . The K salt (m. 210°) seps. as pink needles from a dil. HCl soln., and then m. 181° ; on recrystn. from H_2O the yellow color is restored. HNO_2 does not liberate N but $NaOBr$ liberates 2 atoms. A by-product of the reaction is a double *potassium ammonium salt* of D, $2(PhNBrSO_3K) \cdot PhNBrSO_3NH_4 \cdot H_2O$, pale violet amorphous powder, decomp. 290° . *p*-Bromophenylbiuret-*o*-sulfonic acid, minute, pale violet plates or prisms, decomp. 192° . *Ammonium salt*, hair-like needles, decomp. 194° , or silky, bright yellow needles, decomp. 184° . *Aniline salt*, rhombic plates, decomp. 212° . *Acetate* of E, fine needles, decomp. $269-70^\circ$. From $EtOH$ it seps. as small rhombic or hexagonal plates with 0.5 $EtOH$ of crystn., decomp. 267° . E, boiled with 10 parts Ac_2O for 1.5 hrs., gave *potassium acetyl-p-bromophenylcarbamide-o-sulfonate*, needles with $1H_2O$ of crystn., does not m. 310° . HCl converts this into *p-bromophenylcarbamide-o-sulfonic acid*, also obtained by sulfonation of $BrC_6H_4NHCONH_2$, rhombic plates, contg. 1.5 H_2O , decomp. $256-60^\circ$.

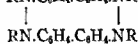
Aniline salt, needles, m. 183–4°. *Benzoate of B*, fine needles, decomp. 192–3°. 2,4-(HO₂S)ClC₆H₄NH₂; *aniline salt*, small rhombic plates, m. 210°. *Potassium p-chlorophenylbiuret-o-sulfonate*, fine pink needles, decomp. 185–90°. The free acid forms pink prisms, decomp. 181–2°. 2,4-(HO₂S)IC₆H₄NH₂: *ammonium salt*, small plates, m. 224–6°. *Aniline salt*, rhombic plates, m. 191.5°. *Potassium p-iodophenylbiuret-o-sulfonate*, pale violet microneedles, decomp. 230–2°. The free acid forms minute gray prisms, decomp. 198°. *Aniline salt*, small, diamond-shaped plates, m. 212–3°. PhNHCN did not condense with HCNO. With ClCO₂Et, PhNKCNC gave phenylcyanourethan, waxy solid, m. 35–5.5°, b₁₀ 160–2° (some decompn.). It is not affected by heating with aq. NH₃ or NH₃ in Et₂O, but is decompd. by heating in a sealed tube 5 hrs. at 110° with alc. NH₃. *Asym-phenylbiuret* in H₂O gave no N on adding HNO₃ and the resulting soln. gave a pale yellow color with alk. β-C₁₀H₇OH. After standing overnight with HNO₃ a red color developed with C₁₀H₇OH. (PhNH)₂CO and AcNHCONHPh behaved in the same way.

C. J. WEST

Organic radicals with quadrivalent nitrogen. III. HEINRICH WIELAND AND FRITZ KÖGL. *Ber.* 55B, 1798–803(1922); cf. C. A. 14, 2637.—It was found in the earlier work that Ph₂NO, the org. analog of NO₂, obtained by dehydrogenation of Ph₂NOH, combines with NO to form a very unstable analog, Ph₂N(:O)NO, of N₂O₄, which by a shifting of the O changes over into Ph₂NNO₂, which further rearranges into *p*-O₂NC₆H₄NHPh. (*p*-MeC₆H₄)₂NO has now been found to give with NO an unstable addn. product, reduced by the catalytic method to (MeC₆H₄)₂NH and NH₃, which is doubtless *di-p-tolynilramine* (A), the first known aromatic representative of this class of compds. Furthermore, it has been found possible to make Ph₂NO react with a deriv. of Ph₂N, the aromatic analog of NO, viz., (*p*-MeOC₆H₄)₂N, which gave Meyer and Gottlieb-Billroth's (MeOC₆H₄)₂NO (B) (C. A. 14, 1533) according to the scheme Ph₂N(:O)N(C₆H₄OMe)₂ → Ph₂NN(:O)(C₆H₄OMe)₂ → Ph₂N + B. In the hope of obtaining a deriv. of Ph₂NO with a basic substituted nucleus, attempts were made to prep. Me₂NC₆H₄NPhOH from *p*-Me₂NC₆H₄NO and PhMgBr but the product was found to consist largely of a substance regenerating Me₂NC₆H₄NO on decomp. with H₂O, and some (*p*-Me₂NC₆H₄N)₂ was also formed as a result of the reducing action of the Grignard compd. The above radical reactions were then extended to Frémy's salt (C) whose violet soln., according to Hantzsch and Semple (*Ber.* 28, 2744(1895)), contains a mol. with 4-valent N, viz., ON(SO₃Na)₂; as it is insol. in all org. solvents, only the addn. of NO could be studied. With carefully purified NO its neutral aq. soln. is quickly decolorized with formation of HNO₂, probably according to the scheme (NaO₂S)₂NO.NO → (NaO₂S)₂NOH + HONO, a reaction which occurs, however, only when the soln. has a chance of becoming faintly acid; if a drop of NH₄OH is previously added, no reaction occurs, whence it is concluded that it is only the free acid which can react as above. With PhNHNH₂ C is decolorized and reduced to HON(SO₃Na)₂ with evolution of N (from the PhNHNH₂), a reaction characteristic of radicals with 4-valent N. *p*-Nitroso-*N*-diphenylhydroxylamine, the intermol. condensation product of PhNO, cannot be dehydrated to the corresponding Ph₂NO deriv. and it is concluded that it does not have the structure ONC₆H₄N(OH)Ph but that, HON·C₆H₄·N(:O)Ph, which has already been assigned to its salts. B, obtained by allowing 2 g. Ph₂NO in satd. Et₂O soln. to stand 12 hrs. with 2.5 g. [(*p*-MeOC₆H₄)₂N]₂ in satd. C₆H₆ soln., m. 161° (M. and G.-B.'s product must have contained some slight impurity, not detectable by analysis, for they describe it as melting 130° and m. 150°). *N-p-Tolyl-N-phenylhydroxylamine* (8 g. from 30.5 g. PhBr and 4.7 g. Mg in Et₂O at –10° slowly treated with 12 g. *p*-MeC₆H₄NO in Et₂O), needles from C₆H₆-gasoline, m. 65–6° (decompn.), sol. in concd. H₂SO₄ with a hissing noise and production of a blue-green color add pptd. by H₂O as a green sulfate, gives in Et₂O at –5° with Ag₂O and Na₂SO₄

p-tolylphenylnitrogen oxide, broad red needles so unstable that they decomp. while being filtered off. C. A. R.

Hydrazines. XXV. A new class of ditertiary aromatic hydrazines. HEINRICH WIELAND AND ALBERT WICKER. *Ber.* 55B, 1804-15(1922); cf. C. A. 15, 70.—While (*p*-MeNHC₆H₄)₂ is oxidized by PbO₂ to the orange-red diimine, MeN:C₆H₄:C₆H₄NMe, it has been found that the sym. diarylbenzidines are converted, without the production of any color, into dehydrogenation products having the compn. but not the mol. wt. nor the properties of diimines. In these cases the removal of H from the sec. N atom does not produce a shifting of the bonds with formation of quinones but there are formed radicals with bivalent N which at once polymerize to colorless ditertiary aromatic hydrazines of a new type, RN.C₆H₄.C₆H₄.NR.



zidines by Zn dust and AcOH; that they are derivs. of tetraphenylhydrazine is shown by the fact that, like the latter, they dissociate in soln. into colored semimers, the ease of dissociation increasing in the order ClC₆H₄, Ph, MeC₆H₄, MeOC₆H₄ for R. The reddish brown color of hot solns. becomes lighter on rapid cooling and returns on again heating; NO, that much-used reagent for N radicals, is taken up by the colored solns. with formation of the bisnitrosamines, [R(ON)NC₆H₄]₂, of the original benzidines. *Bis*(*p*-phenyldibiphenylenehydrazine) (A), from (PhNHC₆H₄)₂ in Me₂CO with powdered KMnO₄ or in C₆H₅N with Ag₂O, cannot be obtained cryst., mol. wt. in boiling CHBr₃, 643, shows blue fluorescence in soln., is not acted upon by 2 N HCl, yields to concd. HCl the deep blue diimmonium salt, dissociates enough to produce an intense color only at the temp. of boiling xylene; long boiling decomp. the radicals resulting from the dissociation into amorphous substances and the benzidines. The [Ph(ON)NC₆H₄]₂ obtained from A in C₆H₅N at 90° with NO or directly from (PhNHC₆H₄)₂ with HNO₂ seps. from C₆H₅N-EtOH in brownish yellow needles m. 158-60° and practically insol. in alc. and Et₂O, while Kehrman and Micewicz (C. A. 7, 348) describe it as m. 124° and being easily sol. in alc. and Et₂O; it loses NO in hot xylene (at 136°) and regenerates the radical which then undergoes further change. *N,N'*-Di-*p*-tolylbenzidine (B), prepd. from *p*-MeC₆H₄NHPh by the method of Marquoyrol and Muraour (C. A. 8, 1568), leaflets from PhMe, m. 233°, gives in H₂SO₄ with NaNO₂ and other oxidizing agents a deep blue color with formation of the merquinoid imonium salt, converted by the method used in prepg. A into *bis*(*p*-tolylidibiphenylenehydrazine), amorphous, m. around 205°, sol. in concd. H₂SO₄ with intense blue color, does not add Ph₃C, mol. wt. in C₆H₆ 2896, gives in C₆H₅N at 90° with NO the *dinitrosamine* of B, fine yellow needles from C₆H₆, m. 188-91° (decompn.). *N,N'*-Di-*p*-anisylhydrazine (C), obtained in 30% yield from MeOC₆H₄NHPh, silvery scales from PhMe, m. 226°; *bis*(*p*-anisylidibiphenylenehydrazine), m. around 200°, dissociates in soln. (even in C₆H₆) with green color, yields with NO at 60° in C₆H₆ the *bisnitrosamine* of C, yellow needles from C₆H₅-EtOH, m. 160° (decompn.). *N,N'*-*Bis*-*p*-chlorophenylbenzidine (D), obtained in 40% yield from Cl-C₆H₄NHPh, leaflets, m. 205°; *bis*(*p*-chlorophenyldibiphenylenehydrazine), m. about 230°; *bisnitrosamine* of D, light yellow needles from C₆H₅-EtOH, m. 193° (decompn.). The quinobenzidine obtained by rearrangement from the hydrazine of tetrahydroquinoline (W. and Haas, C. A. 15, 70) likewise gives with Ag₂O in C₆H₅N a *bishydrazine*, C₈H₈N₄, m. about 172°, shows the red-brown color of the dissociated radical appreciably only at the temp. of boiling BzOEt, slowly dissolves in AcOH with olive-brown color soon changing to green, decomp. in concd. HCl, mol. wt. in CHBr₃ 1097. C. A. R.

The sulfur content of arspenamine and its relation to the mode of synthesis and toxicity. III. W. G. CHRISTIANSEN. *J. Am. Chem. Soc.* 44, 2334-42(1922); cf. C. A. 16, 1833.—In reducing 4,3-HO(O₂N)C₆H₃AsO₃H₂ to arspenamine the toxicity, and S content of the products are practically the same whether com. or purified Na₂S₂O₄ is

used and the formation under certain conditions of relatively toxic products with a high S content is therefore not due to impurities in the com. $\text{Na}_2\text{S}_2\text{O}_4$. The products are also fairly uniform in regard to toxicity and S content irrespective of the period of formation during the reduction. Aminohydroxyarseno compds. in general contain the fewest S atoms when prepd. from the NH_2 acids. Fixation of the hydroxyl H in the nitrohydroxy-arsenic acids tends to make the $\text{Na}_2\text{S}_2\text{O}_4$ reduction abnormal and the products, when they can be isolated, contain more S than analogous substances prepd. without fixation of this H atom. The hydroxyl H in the *o*-position to the NO_2 group seems to play an important role in the formation of arseno compds. of the type under consideration. Probably the SO_3H group found in certain samples of arspenamine enters the ring by way of the N atom with the intermediate formation of a sulfamic acid. *3-Nitro-4-methoxyphenyl-arsonic acid* is obtained in 94% yield from *p*- $\text{MeOC}_6\text{H}_4\text{AsO}_3\text{H}_2$ nitrated at 0° in H_2SO_4 with 1 mol. HNO_3 dild. with an equal vol. of H_2SO_4 , then allowed to rise to 10° and dild. with 4 vols. H_2O . *3-Nitro-4-hydroxy-5-methylphenylarsonic acid*, similarly prepd. from $\text{Me}(\text{HO})\text{C}_6\text{H}_3\text{AsO}_3\text{H}_2$, fine yellow needles; yield, 81%. *4-Methoxy-5-methylphenyl-arsonic acid*, obtained in 75% yield from 5,4-Me($\text{HO})\text{C}_6\text{H}_3\text{AsO}_3\text{H}_2$ and alk. Me_2SO_4 , needles from H_2O , does not m. 260° , gives on nitration as above the 3-nitro acid, fine pale yellow needles; yield, 70%. *3-Nitro-3-carbomethoxyphenylarsonic acid*, coarse yellow prisms from H_2O ; yield, 75%. 2,4-($\text{MeO})_2\text{C}_6\text{H}_3\text{AsO}_3\text{H}_2$, stout needles from 50% AcOH , m. $238-9^\circ$, is obtained in 7.4 g. yield from 25 g. of the di-HO acid with alk. Me_2SO_4 , and on nitration gives 77% of the 3-nitro acid, feathery needles with a slight tinge of greenish yellow. *3-Acetamino-4-methoxyphenylarsonic acid* (7.9 g. from 7.8 g. of the 4-HO acid and Me_2SO_4 in NaOH), gives on hydrolysis with HCl on the H_2O bath and reduction with $\text{Na}_2\text{S}_2\text{O}_4$ in the presence of MgCl_2 3,3'-diamino-4,4'-dimethoxyarsenobenzene, isolated as the dihydrochloride (A), yellow powder with $2\text{H}_2\text{O}$, sol. in H_2O with yellow color, gives with excess of NaOH a yellow ppt. dissolving without color when oxidized with I_2 , gives with Na_2SO_4 and NaOAc ppts. of the sulfate and base, resp., forms with *p*- $\text{Me}_2\text{NC}_6\text{H}_4\text{CHO}$ an orange ppt., gives, when diazotized in HCl , a yellow soln. coupling in alc. with $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2\cdot\text{HCl}$ to a deep purple dye, is gradually reddened in soln. by FeCl_3 . When 4,3-MeO($\text{O}_2\text{N})\text{C}_6\text{H}_3\text{AsO}_3\text{H}_2$ (B) is reduced with $\text{Na}_2\text{S}_2\text{O}_4$ under the conditions most favorable for the production of arspenamine from the NO_2 acid, only a very slight ppt. of arseno base is obtained. If, after the reduction, the soln. is cooled to room temp. and treated with NaCl (35 g. per 2.1 g. A) a yellow ppt. forms which, treated with HCl in MeOH and pptd. with Et_2O , gives a product qual. like A but contg. 3.47% S; yield, 1.3 g. from 2.1 g. B. 3,3'-Diamino-4,4'-dihydroxy-5,5'-dimethylarsenobenzene dihydrochloride, obtained in 2.6 and 2.9 g. yield from 4.2 g. 5,4,3-Me($\text{HO})\text{C}_6\text{H}_3\text{AsO}_3\text{H}_2$ with $\text{Na}_2\text{S}_2\text{O}_4$ under the conditions most and least favorable, resp., for the formation of arspenamine from the NO_2 acid, seps. with $2\text{H}_2\text{O}$, judging from the As content. Reduction of 5,4,3-Me($\text{MeO})\text{C}_6\text{H}_3\text{AsO}_3\text{H}_2$ proceeds exactly like that of B, 2.2 g. of the acid yielding 1.3 g. of the di-HCl salt of the arseno compd.; S content 3.68%. 3,3'-Diamino-4,4',6,6'-tetramethoxyarsenobenzene dihydrochloride is similarly obtained in 1.4 g. yield from 2.3 g. of the arsenic acid.

C. A. R.

Condensation products of arspenamine with aldehydes. G. W. RAIZISS AND A. C. BLATT. *J. Am. Chem. Soc.* **44**, 2023-7 (1922).—When (3,5- $\text{ClH}_2\text{H}_2\text{N}(\text{HO})\text{C}_6\text{H}_2\text{As}$)₂ (A) in MeOH is converted into the di-Na salt by adding 4 mols. aq. NaOH , then treated with slightly more than 2 mols. of an aldehyde and in some cases stirred, in others boiled, 2 hrs. in a N atm. and neutralized with dil. HCl there are obtained condensation products of the type $[\text{RCH}(\text{OH})\text{NH}(\text{HO})\text{C}_6\text{H}_2\text{As}]_n$, which are unstable substances readily decompd. by acids and even more so by alkalis. The following 4,4'-dihydroxyarsenobenzenes were prepd. in this way: 3,3'-Bis-[α , α -dihydroxybenzyl-amine] (16 g. from 14.25 g. A and 8 g. *o*- $\text{HOC}_6\text{H}_4\text{CHO}$), yellowish brown ppt., m. 182° ,

sol. in NaOH, insol. in dil. mineral acids; the deep red alk. soln. turns yellow on standing and evolves the odor of the aldehyde; *dihydrochloride*, orange-yellow ppt. from MeOH-Et₂O. 3,3'-*Bis*-[α -hydroxy-*p*-methoxybenzylamino] (1.5 g. from 4.75 g. A and 2.2 mols. *p*-MeOC₆H₄CHO), yellow powder, begins to soften 80°, gradually decomp. on higher heating. 3,3'-*Bis*-[ρ , α -dihydroxy-*m*-methoxybenzylamino], obtained in 64.5% yield from vanillin, reddish brown amorphous solid from MeOH-Et₂O, m. 175-6°, sol. in NaOH or Na₂CO₃ with a red color turned yellow by an excess of the solvent, especially on warming, insol. in NaHCO₃. 3,3'-*Bis*-[(hydroxymethyl)amino], obtained in 44% yield from A in MeOH with 2 mols. HCHO and 5 mols. of *N* HCl, begins to decomp. 185°. 3,3'-*Bis*-[α -hydroxy-*m*-nitrobenzylamino], from *m*-O₂NC₆H₄CHO (yield, 35%), yellow powder, decomp. 247-50°, sparingly sol. in dil. NaOH, gradually decomp. 3,3'-*Bis*-[α -hydroxy- γ -phenylallylamino], obtained in 50% yield from PhCH:CHCHO, yellow ppt., decomp. 195-200°, forms a reddish brown ppt. with dil. mineral acids. C. A. R.

Synthesis of aromatic arsonic acids. HEINRICH BART. *Ann.* 429, 55-103(1922).—Aromatic arsonic acids result, according to Ger. pat. 250,264, by the interaction of diazo compds. and H₃AsO₃ or its salts. The course of the reaction and the yield of the aryl-arsonic acid depend upon the H or I/O ion concn. and the diln. of the reaction mixt. In the case of PhAsO₂H₂, it is shown that the yield decreases with the increasing amt. of NaOH present. It is often convenient to work in dil. soln., since side reactions often occur when concd. solns. are used. The prepn. of PhAsO₂H₂, 2-, 3-, and 4-MeC₆H₄-AsO₂H₂, 4-EtOC₆H₄AsO₂H₂, 4-AcNHC₆H₄AsO₂H₂, 4-ClC₆H₄AsO₂H₂, 4-HOCC₆H₄-AsO₂H₂, C₆H₄(AsO₂H₂)₂, 4-HOCC₆H₄AsO₂H₂, 3,4-HO(O₂N)₂C₆H₃AsO₂H₂, all of which have been described before, is given in detail. 2-Chlorophenylarsonic acid, from *o*-ClC₆H₄N₂Cl and Na₂HAsO₃, needles from H₂O, m. 181°. 3-Chloro derivative, m. 175°. 2-Carboxyphenylarsonic acid, from 2-HOCC₆H₄N₂Cl, after extg. impurities with MeOH, leaflets, which do not m. 300°. 3-Carboxy derivative, needles which form an anhydride above 250°. 2-Hydroxy derivative, m. 191°; sodium salt, easily sol. in H₂O and salted out with difficulty by NaCl. 2-Nitro derivative, needles, m. 233°. Of the 3 isomers this is the most insol. in H₂O. 3-Nitro derivative, m. about 200° with anhydride formation. 4-Nitro derivative, m. about 300° (decompn.), *sym*-2,4-(O₂N)₂C₆H₃N₂OH and Na₂AsO₂H give a good yield of the arsonic acid (Ger. pat. 266,944), but in a strongly acid soln. little or no reaction occurs. 5-Nitro-2-hydroxyphenylarsonic acid, from 4,2-O₂N(H₂N)C₆H₃OH, pale yellow prisms, decomp. about 250°. 2-Nitro-4-hydroxy derivative, yellow needles, m. 228°; the alkali salts are a deep yellow. Diphenylarsonic acid, by the reaction of PhN₂Cl and PhAsO₂, needles, m. 178°. 4-Nitrophenylarsonic acid, by the action of SO₂ upon 4-O₂NC₆H₄AsO₂H₂, yellow powder which explodes without m. 4,4-Dinitrodiphenylarsonic acid, from 4-O₂NC₆H₄N₂Cl and O₂NC₆H₄As(OH)₂, yellow powder, m. 278°. C. J. Wrsr

Formation of aromatic arsonic acids through the reaction of isodiaz compounds with arsenic acid ion. HEINRICH BART. *Ann.* 429, 103-13(1922); cf. preceding abstr.—Contrary to the results of Gutmann (*C. A.* 6, 1619), B. finds that the antediazo hydrates react with the arsenate ion with the formation of aromatic arsonic acids. It is necessary to have a low HO⁻ concn., secured by passing CO₂ into the soln. or by the addition of bicarbonate. The reaction was studied with the 2-, 3-, and 4-NO₂ deriv. and the 2- and 4-HO₂C deriv. C. J. Wrsr

Two new syntheses of 3,3'-diamino-4,4'-dihydroxyarsenobenzene (so-called salvarsan base). HEINRICH BART. *Ann.* 429, 113-22(1922); cf. preceding abstr.—There are two difficulties in the synthesis of (3,4-H₂N(HO)C₆H₄As)₂ (A): obtaining a pure 3-NO₂ deriv. for reduction and a suitable reducing agent. The following 2 methods avoid these difficulties. 4-Hydroxyphenylarsonic acid-3-azobenzene, by the action of Na₂AsO₂H upon the diazo compd. from 4,2-(H₂N)(HO)C₆H₃N:NPh, purified through the Na salt,

bronze glistening leaflets; reduction of the Na_2CO_3 soln. by $\text{Na}_2\text{S}_2\text{O}_3$ and MgCl_2 at 60° gives a good yield of A. 2-Carbethoxyamino-4-nitrophenol, by the reaction of CO_2ClEt upon 4,2-(O_2N)(H_2N) $\text{C}_6\text{H}_3\text{OH}$ in $\text{C}_6\text{H}_5\text{N}$, m. 208° . This is reduced and the crude product diazotized and transformed into 3-carbethoxyamino-4-hydroxyarsonic acid, needles, decomp. about 200° . 3,3'-Dicarbethoxyamino-4,4'-dihydroxyarsenobenzene is formed by the action of H_3PO_2 at 100° in an atm. of CO_2 , and is saponified by 45% KOH in an atm. of H to A.

C. J. WEST

A sulfonated naphthylarsonic acid. A. E. HILL AND A. K. BALLS. *J. Am. Chem. Soc.* 44, 2051-4 (1922).— $\alpha\text{-C}_{10}\text{H}_7\text{AsO}_3\text{H}_2$, needles from H_2O , m. 197° , was prepd. by diazotizing $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2$ in aq. HCl and allowing the diazotized soln. to stand several days with Na_2AsO_4 ; this stirred 1 hr. with about 6 parts of fuming H_2SO_4 (d. 1.9) gives 60% of a sulfo- α -naphthylarsonic acid, somewhat hygroscopic plates from H_2O , insol. in mineral acids, does not m. or decomp. below 250° , oxidized by alk. KMnO_4 ; alc. exts. from the residue obtained by evap. the oxidized soln. a thick yellow hygroscopic liquid with 4.08% H_2O , 15.90% As and 6.75% S and giving with resorcinol- H_2SO_4 the fluorescence tests for the phthalic acid configuration. Three K salts of the acid were prepd. by adding the calcul. amts. of K_2CO_3 to the acid; only the mono-K salt was recrystd. for analysis.

C. A. R.

The purification of naphthenic acids. FRANZ ZERNIK. *Z. angew. Chem.* 35, 566-7 (1922).—A review. The prepn. and purification of satd. O acids from crude petroleum and the medicinal and technical uses of the acids, esters and salts are described.

C. C. DAVIS

Aromatic antimony compounds. VI. Mutual transformation of mono-, di- and triarylaminty compounds. HANS SCHMIDT. *Ann.* 429, 123-52 (1922); cf. *C. A.* 16, 3076.—*p*-Acetylaminophenylstibine chloride hydrochloride (A), prepd. by reducing the acid in HCl with SnCl_2 , sinters 125° . It slowly decomp. in a closed vessel, AcOH being split off by the liberated HCl. MeOH splits off the HCl, giving the free stibine chloride, $\text{AcNHC}_6\text{H}_4\text{SbCl}$, m. 200° . $\text{N NH}_4\text{OH}$ transforms the HCl salt into the oxide, $\text{AcNHC}_6\text{H}_4\text{SbO}_2\cdot\text{H}_2\text{O}$, amorphous, sinters 180° . Heated 3 hrs. with MeOH, the oxide gives *p*-triacetylaminotriphenylstibine, $(\text{AcNHC}_6\text{H}_4)_3\text{Sb}$; this exists in 3 forms: The A-modification (A') crystals from MeOH in needles, contains 0.5 mol. H_2O , sinters 205° , m. about 270° . Crystd. from anhydrous AcMe or heated with C_6H_6 , it gives the B-modification, m. 268° ; the A-form results by heating with MeOH. When the A-form is heated with AcMe containing some H_2O , the C-form results, sinters 225° , contains $\frac{1}{2}$ mol. H_2O , and is transformed into the A-form by heating with MeOH. A MeOH soln. of A, quickly cooled, and treated with 3% H_2O_2 , gives the stibine hydroxide (B), best isolated by forming the chloride with HCl, pptg. with H_2O , liberating the base with NaOH and crystg. from dil. MeOH, m. 200° . From anhydrous MeOH a 2nd modification is obtained which m. 250° . B is insol. in alkali. A is transformed by alc. HCl into *p*-diacetylaminodiphenylstibine chloride hydrochloride (C), m. about 135° . This is unstable and slowly decomp., with the splitting off of HCl and then AcOH. 5 N NaOH acting upon a MeOH suspension of C transforms it into the oxide (D), contg. 1.5 H_2O , m. 130° . *p*-Diacetylaminodiphenylstibinic acid, $(\text{AcNHC}_6\text{H}_4)_2\text{SbO}_2\cdot\text{H}_2\text{O}$, results by the oxidation of D in MeOH with 3% H_2O_2 or by the oxidation of A in 2 N NaOH with 3% H_2O_2 , powder, m. $230\text{--}5^\circ$. HCl ppts. a chloride, while an acetate, m. 205° , crystals from the AcOH soln. D, dissolved in AcOH and treated with concd. HCl in the cold, gives A'. PhSb , heated in an atm. of CO_2 with alc. HCl, gives Ph_3SbOH , best isolated through the acetate, needles, m. 132° . Characteristic of the oxide is the pptn. of a voluminous sulfate from an Et_2O soln. and of an oxalate from an Et_2O , AcMe or EtOH soln. The decompn. is dependent upon exptl. conditions. In the air considerable amts. of Ph_3SbCl_2 are formed, while with aq. HCl, Sb is split off. Ph_3Sb , heated

with dil. NaOH and 3% H_2O_2 , then treated with HCl, gives $PhSbCl_3 \cdot H_2O$. In the absence of alkali (AcMe), H_2O_2 gives $PhSb(OH)_3$, isolated as the *diacetate*, m. 215°, which may be transformed into $PhSbCl_3$ by alc. or concd. aq. HCl, m. 142°. $PhSbOH$ is transformed by boiling with AcOH or HCO_2H into $PhSbO_2H$; the same change occurs with satd. alc. HCl in an atm. of CO_2 . $PhSb<$ may be changed into $PhSb<$ derivs. by alc. HCl. *p*-Aminophenylstibinic acid, $[3(H_2NC_6H_4SbO_2) \cdot 3H_2O] \cdot 4H_2O$, results by the sapon. of the Ac deriv. with 5 *N* NaOH, powder, easily sol. in dil. NaOH, from which alc. ppts. a voluminous Na salt. With ice-cold HCl it forms a *tetrachloride hydrochloride*, $C_6H_7NC_4Sb_2H_2O$, dark colored powder, m. about 155°, easily sol. in H_2O . *p*- $HOC_6H_4N_2Cl$ and Sb_2O_3 give *p*-hydroxyphenylstibinic acid, $[3(HOC_6H_4SbO_2) \cdot H_2O] \cdot 6H_2O$, purified through the C_6H_5N salt, powder, does not m. 270°, sol. in hot H_2O and giving a violet color with $FeCl_3$. The *pyridine double salt* is yellow, stable in the air and m. 176°. The *p*-ethoxy derivative is formed from *p*- $EtOC_6H_4NH_2$, powder with the odor of $PhOH$ does not m. 270°; it gives a chloride, which decomps. within 24 hrs. *m*-Amino-*p*-hydroxyphenylstibine chloride hydrochloride, by reduction of the NO_2 deriv. with $SnCl_2$, m. 165-70°. Treated in dil. AcOH with HPO_3 and $NaPO_3$, it yields *m,m'*-diamino-*p,p'*-dihydroxystibiobenzene, dark brown powder, sol. in dil. NaOH or HCl. C. J. W.

Interaction of aldehydes or ketones and thiocarbamides in the presence of acids. II. JOHN TAYLOR. *J. Chem. Soc.* 121, 2267-72 (1922); cf. C. A. 11, 1645.—The reaction of $(NH_4)_2CS$ and BzH gave a product, $C_6H_5N_2S$, m. 176-7°, and a H_2O -sol. part, from which picric acid ppts. an impure *picrate*, m. 144-6°. *o*- HOC_6H_4CHO and $(NH_4)_2CS \cdot HCl$ combine slowly (4 months); $POCl_3$ causes considerable condensation in 2 days; *thiourea-salicylaldehyde picrate* decomps. 166-8°. This reaction also gave an insol. part, which is a complex condensation product with 10.8% S. *Thiourea-cinnomonaldehyde picrate*, m. 184°. *Sulfate*, amorphous powder, m. 171-3°. NH_3 liberates a cream-colored base, decomp. 122°. *Thiourea-acetone picrate*, hexagonal plates, m. 193-4°. *Thiourea-acetophenone picrate*, m. 168-74°. *Phenylthiourea-acetone picrate*, m. 190-1°. C. J. WESR

Chlorination and bromination of the toluic acids and the preparation of the phthalaldehydic acids. WM. DAVIES AND WM. H. PERKIN, JR., with H. CLAYTON. *J. Chem. Soc.* 121, 2202-15 (1922).—*o*-Bromo-*o*-toluyl bromide, prepd. by slowly dropping Br into MeC_6H_4COCl at 185-95°, b_{72} 170-1°, needles, m. 33-4°. Added to $EtOH$, it gives *ethyl o-bromo-o-toluate*, heavy oil, which decomps. at 30 mm. with elimination of $EtBr$ and the formation of phthalide. When the ester stands with dil. $EtOH \cdot NH_3$ for several days, phthalimidine results. Shaken with NaI in $AcMe$, the ester gives *ethyl o-iodo-o-toluate*, microneedles, m. 32.5°. It does not appear to react smoothly with Mg . The reaction with KCN , followed by HCl , gives $C_6H_4(CHCO_2Et)CO_2Et$. The reaction of the Br ester with $CNCHNaCO_2Et$ gave a high boiling fraction, b_{18} 280-2°, which was not further examd., and *ethyl α -cyano-o-carbethoxy- β -phenylpropionate*, needles, m. 38-40°, which upon treatment with cold concd. H_2SO_4 for 24 hrs., gives *ethyl o-carbethoxybenzylmalonic acid*, glistening needles, m. 132°. *o*-Bromo-*m*-toluyl bromide, b_{72} 167°. *Ethyl o-bromo-m-toluate*, b_{70} 174-5° and has a peculiar sour odor. The Cl acid chlorides were prepd. by chlorinating the acid chloride in bright light 1st at 160° and then at 210°. 40 g. may be treated in 3 hrs. The esters are prepd. by treating with an excess of alc., while the free acids are obtained by warming the chlorides with 6 times their wt. of HCO_2H . *o*-Dichloro-*o*-toluyl chloride, thick, glassy prisms, m. 27-8°, b_{72} 151°, b_{740} 267-9°. The free acid forms glistening needles, m. 155°. *Ethyl ester*, mobile liquid with pungent but pleasant, fruity odor, b_{74} 172°; under ordinary pressure $EtCl$ is split off with the formation of α -chlorophthalide. *Amide*, glistening prisms, m. 117°. When heated at 140°, HCl and a black tar are produced; HCl is also eliminated by boiling with H_2O or C_6H_5N . *o*-Dichloro-*m*-toluyl chloride, long needles, m. 48-9°, b_{718}

280–2°. The acid seps. from CHCl_3 as microprisms, m. 132°. *Ethyl ester*, liquid. The *p*-chloride forms microneedles, m. 44–5°, b_{114} 285–6°. The acid crysts. in microneedles from HCO_2H or in short, thick prisms from C_6H_6 , m. 151–8°. *Ethyl ester*, small, thin prisms, m. 45–6°. Continued chlorination gives the tri-Cl derivs. The temp. must be increased to 240° and the time to 10 hrs. ω -Trichloro-*o*-toluyl chloride, b_{114} 285–8°, b_{115} 145–55°, m. 87°. This is identical with the phthalic acid tetrachloride of Vongerichten (*Ber.* 13, 447). *Ethyl ester*; this easily loses EtCl , giving *s*- $\text{C}_6\text{H}_4(\text{COCl})_2$. The free acid forms needles from C_6H_6 , m. 141–4°. The *m*-chloride b_{114} 287°. *Methyl ester*, needles, m. 55°. The free acid forms sparkling laminas, m. 142°. The *p*-chloride b_{114} 296°. The free acid forms minute plates m. 196–7°. Boiled 5 min. with HCO_2H , it is completely converted into terephthalic acid. *Methyl ester*, long attenuated plates, m. 55°. *Ethyl ester*, plates, m. 57°. *Amide*, needles, m. 180°. One of the most valuable uses of the ω - $\text{Cl}_3\text{CHC}_6\text{H}_4\text{COCl}$ has resulted from the discovery that they serve as a very convenient source of $\text{C}_6\text{H}_4(\text{CO}_2\text{H})\text{CHO}$, the process consisting in simply digesting them with $\text{Ca}(\text{OH})_2$ or CaCO_3 in an inert atm. The yields are about 70%. C. J. WEST

p-Dithiobenzoic acid. SAMUEL SMILES AND D. C. HARRISON. *J. Chem. Soc.* 121, 2022–6 (1922).— $\text{HO}_2\text{CC}_6\text{H}_4\text{SO}_2\text{Na}$, contg. 2 H_2O , is conveniently prepd. by oxidizing $\text{MeC}_6\text{H}_4\text{SO}_3\text{Na}$ with KMnO_4 ; the anhyd. salt (dried at 125–30°) is heated with ClSO_3H at 100° for 1 hr., giving *p*-chlorosulfonylbenzoic acid (A), needles, m. 235° (decompn.). With Na_2SO_3 this yields *p*-sulfinobenzoic acid, needles, m. about 245° (decompn.). The reduction of A in AcOH with Zn and concd. HCl leads to the formation of *p*-thiolbenzoic acid, powder, decomp. about 250°, sparingly sol. in all common solvents, and very susceptible to oxidation. It was characterized by conversion into the Me deriv. *p*-Dithiobenzoic acid, powder, decomp. above 320°. Preliminary expts. indicate that the acid is decompd. by NaOH , the reaction being much more rapid than in the case of the *o*-compd. C. J. WEST

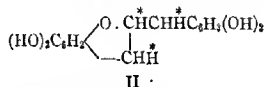
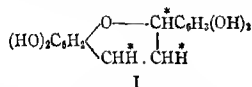
Sulfoacetic acid as a condensing agent. IV. Isoacetovanillone. WILHELM SCHNEIDER AND EDGAR KRAFT. *Ber.* 55B, 1892–9 (1922); cf. *C. A.* 16, 1248.—This report of the results of the extension of the sulfoacetic acid method to guaiacol (A) is published now in view of the appearance of the paper of Brand and Collischonn (*J. prakt. Chem.* 103, 333 (1922)). If the A is treated with Ac_2O contg. sulfoacetic acid (B) in the manner previously described for PhOMe there results a dark soln. from which a 4-methylpyrylium compd. corresponding to that obtained with PhOMe can be isolated. By interrupting the reaction after several hrs., however, 3-acetoxy-4-methoxyacetophenone (acetylisoacetovanillone) (C) can be obtained in considerable yield. Thus, 50 g. A allowed to stand 5 hrs. in an "acetylating mixt." (prepd. from 350 cc. Ac_2O and 50 cc. concd. H_2SO_4 heated to 80° and cooled to room temp.) gives about 20 g. C, leaflets or fine needles from H_2O , m. 66°, quite stable towards boiling H_2O , hydrolyzed by boiling aq. alkali to 3-hydroxy-4-methoxyacetophenone (isoacetovanillone) (D), crystals with 1 H_2O , m. 66–9° and, anhyd., 91°, sol. in concd. HCl and H_2SO_4 with yellow, in concd. HNO_3 with red color, gives a blue-violet color with FeCl_3 ; *oxime*, fine needles from H_2O , m. 138°; *semicarbazone*, m. 206°. $\text{Me}_2\text{SO}_4\text{-NaOH}$ converts D into acetoveratrone, m. 49–50°. A (20 g.) refluxed 1.5 hrs. in 40 g. Ac_2O contg. 2 drops concd. H_2SO_4 gives only acetylguaiacol and PhOMe under the same conditions remains unchanged. C. A. R.

Condensation of certain nitriles and various polyhydroxyphenols to form phenolic acids. W. D. LANGLEY WITH ROGER ADAMS. *J. Am. Chem. Soc.* 44, 23, 20–30 (1922).—In attempting to apply the Hoesch ketone synthesis to resorcinol and $\text{ClCH}_2\text{CH}_2\text{CN}$, it was found that the reaction proceeded abnormally and instead of a ketone there was formed an acid according to the scheme: $\text{C}_6\text{H}_3(\text{OH})_2 + \text{ClCH}_2\text{CH}_2\text{CN} \longrightarrow (\text{HO})_2\text{C}_6\text{H}_2\text{-CH}_2\text{CH}_2\text{CN} \longrightarrow (\text{HO})_2\text{C}_6\text{H}_2\text{CH}_2\text{CH}_2\text{C(=O)NH} \longrightarrow \text{HOOC-C}_6\text{H}_2\text{-CH}_2\text{CH}_2\text{C(=O)NH.HCl} \cdot \text{O}$

→ 2,4-(HO)₂C₆H₃CH₂CH₂CO₂H (A). The A, obtained in 56% yield, m. 165°, and is identical with the product obtained by reduction of umbelliferone (although Hlasiwetz, *Ann.* 139, 102(1866), states that it decomps. above 110°); it can also be obtained from *m*-C₆H₄(OH)₂ and CH₂:CHCN in Et₂O with ZnCl₂ and HCl. Lactone of A, from the reaction product of C₆H₄(OH)₂, ClCH₂CH₂CN, ZnCl₂ and HCl in Et₂O treated with cold H₂O, or from A heated 2 hrs. at 130-5°, cubes from PhMe, m. 132-3°, insol. in cold hut sol. in hot Na₂CO₃ with formation of A; acetate of the lactone (9 g. from 7 g. A heated 1 hr. on the H₂O bath in 10 g. Ac₂O), m. 111-2°, hydrolyzed to A by hot H₂O or Na₂CO₃. β-2,4-Dimethoxyphenylpropionic acid, obtained in 68% yield from A with alk. Me₂SO₄, m. 102.5-3.5°, undoubtedly identical with the reduction product, m. 105°, of dimethoxyumbellelic acid (Will, *Ber.* 16, 2116(1883)). β-[5-Nitroso-2,4-dihydroxyphenyl]propionic lactone (4 g. from 3 g. A in alc. with 4 g. BuONO and concd. HCl), cream-colored solid, m. 147.5-8.0° (decompn.). β-[2-Hydroxy-4-methoxyphenyl]propionic acid, from *m*-MeOC₆H₄OH and ClCH₂CH₂CN with ZnCl₂ and HCl in Et₂O, m. 138-9.5; the lactone is an oil. The Et₂O soln. decanted off from the crude reaction product in the prepn. of the acid yields on evapn. *in vacuo*, besides unchanged MeO-C₆H₄OH, β-[2-hydroxy-4-methoxyphenyl]propionitrile, m. 126.5-7.5°, insol. in Na₂CO₃ sol. in NaOH, recovered unchanged on acidification, but hydrolyzed to the acid on boiling. γ-2,4-Dihydroxyphenylbutyric acid, obtained in 20.8% yield from C₆H₄(OH)₂ and ClCH₂CH₂CH₂CN, crystals with 1 H₂O, m. 89-99°, and anhyd. plates from C₆H₆, m. 118.5-9.0°, m. forms no lactone when heated 0.5 hr. at 133-4°. β-[2,4-Dihydroxy-6-methylphenyl]propionic lactone (1.7 g. from 5 g. orcinol and 5 g. ClCH₂CH₂CN or 3.6 g. from 5 g. orcinol and 2.3 g. CH₂:CHCN), m. 149-1.5°, sol. in hot alkali and repptd. on acidification. β-2,4,6-Trihydroxyphenylpropionic lactone (about 5 g. from 5 g. phloroglucinol and 5 g. ClCH₂CH₂CN), viscous oil sol. in hot Na₂CO₃ and repptd. by acids.

C. A. R.

Tannins and similar compounds. IX. Stereoisomeric catechols. II. KARL FREUDENBERG, OTTO BÖHME AND LUDWIG PURRMANN. *Ber.* 55B, 1734-47(1922); cf. C. A. 16, 356.—Recent work on catechol (A) has led to the conclusion that it is derived from either I or II by substitution of HO for one of the starred H atoms.



If this HO group is attached to one of the C atoms which also carries another H atom, the A will then contain 2 asym. C atoms and must be capable of existing in 2 *dl*-forms besides the corresponding active forms, but if the HO group is on the C atom carrying the bridge O atom, the A will contain only 1 asym. C atom. This last possibility is excluded as follows: It had already been found that the free *d*-A is racemized with relative ease, and if it contains 2 asym. C atoms, then, in its rearrangement, before the racemization is complete there must be present, besides the original *d*-A and its racemate, a new racemate and 1 of its active components. As there seemed to be but little hope of sepg. such a mixt. of 4 substances, however, the rearrangement was carried out with the *dl*-A, and although a large part of it resinified, as many hrs.' boiling in NaCl was required, the remainder consisted of a mixt. of 2 inactive catechols which it was found possible to sep. The new compd. is designated *dl*-epicatechol (B). B having once been isolated, it was possible to establish its presence in *pegu* catechu, as well as that of its *l*-form (C). It is recognized that in the above views there are 2 points open to attack; viz., it remains to be proved that C is really the *l*-form corresponding to B and that A and B are in truth stereoisomers and not structural isomers, but all the evidence at present available harmonizes with the views given above. From 20 g. *dl*-A boiled 24

hrs. in satd. NaCl in H or CO₂ and exhd. 10 hrs. with Et₂O, the residue from the Et₂O being then taken up in 20 cc. H₂O and allowed to cryst. at 10°, is obtained 1.3 g. unchanged *dl*-A, while the mother liquors, purified with Ph(OAc)₂ as described below, concd. *in vacuo* to 10 cc. and allowed to cryst. at 0° yield 0.8 g. B. When finely ground acacia (pegu) catechu, mixed with an equal vol. of sea sand, is exhd. 30–36 hrs. with Et₂O, the Et₂O evapd., the residue taken up in 4 parts hot H₂O and allowed to cryst. at room temp., the mother liquors and washings concd. *in vacuo* and again allowed to cryst., the process repeated as long as crystals sep. at 18°, the individual crops taken up in 3 parts hot H₂O, treated with 0.01–0.02 vol. of 15% Pb(OAc)₂, filtered hot, freed from Ph with H₂S and allowed to cryst. at 0°, the successive crops are found to consist of *dl*-A with increasing amts. of *l*-A (4–5% of the catechu used), then of C and finally of B. The crude crystals can also be purified by dissolving in Me₂CO, nearly decolorizing with Al₂O₃, evap. *in vacuo* and recrystg. from H₂O at 0°. C, fine needles with 3H₂O, decompds. around 228°, [α]_D²⁰ yellow –38.4° (50% Me₂CO), –41.2° (96% alc.); *pentaacetate*, needles from alc., m. 123–9°, [α]_D²⁰ yellow –28.6° in (CHCl₃)₂. B crystals below 10° in thick plates more sol. than any other known catechol, changing when heated with a little H₂O at 40–50° into less sol. needles, very hygroscopic when dehydrated, m. 240° (decompn.); *pentaacetate*, m. 169–72°. Rhubarb catechol (0.2 g. from 100 g. Chinese rhubarb), proved to be pure *d*-A, [α]_D²⁰ yellow 18.0° (50% Me₂CO). In the product from steamed mahogany (less than 1% of the wood) were identified *d*- and *dl*-A, and *d*-epicatechol also was probably present; the catechol from *Paullinia* (2.5 g. from 100 g. Chinese guarana paste) behaved like that from mahogany. The pentaacetates of the 4 catechols easily lose the 4 Ac residues on the phenolic HO groups (best on boiling in alc. with KOAc), while the 5th Ac group on the sec. aliphatic HO is not removed. *Monoacetyl-d-catechol*, obtained in 80% yield from 3 g. of the pentaacetate boiled 5 hrs. in H with 11 g. KOAc in 250 cc. abs. alc., needles with 2H₂O, m. (anhyd.) 120–5°, [α]_D²⁰ yellow –19.9° (50% Me₂CO); all attempts to remove the Ac group with NaHSO₄, Na₂CO₃, piperidine, PhNH₂ or tannase either led to complete decompn. or left the acetate unchanged; a not too dil. aq. soln. ppts. 0.5% gelatin more than does *d*-A. Tetramethyl-*d*-catechol (D), crystd. from alc. (10 times) and CCl₄ (2 times) to constancy of m. p. and rotation, m. 146–7°, [α]_D²⁰ –12° in (CHCl₃)₂, dissolves in concd. H₂SO₄ with a yellow to deep orange color (depending on the concn.) changing in the course of 0.5 hr. through green to deep violet. Pentamethyl-*d*-catechol, crystd. once from EtOH, 8 times from AmOH and finally from MeOH, m. 92–3°, [α]_D²⁰ 8.2° in (CHCl₃)₂ sol. in concd. H₂SO₄ with faintly yellow color changing in 0.5 hr. through blue-green into violet. Tetramethylmonoacetyl-*d*-catechol, from D with Ac₂O in C₂H₅N, recrystd. 8 times from AmOH and 4 times from MeOH, m. 95–6°, [α]_D²⁰ 5.8° in (CHCl₃)₂. *d*-A usually crysts. with 4H₂O, but when the ordinary product is stirred about 1 hr. at 50° with 18 parts H₂O there remains a few % in the form of anhydrous needles, [α]_D²⁰ yellow 16.9° (in 50% Me₂CO), shows no rotation in 96% alc., is converted into the tetrahydrate when crystd. from a little H₂O and Pb(OAc)₂, gives on acetylation the pentaacetate, m. 132°, [α]_D²⁰ 39.4° in (CHCl₃)₂. One part of 1% *d*-A still gives a turbidity with 2 parts of 0.5% gelatin at room temp. and a ppt. at 10°; with brucine in AcOH it yields the addn. compound C₁₅H₁₄O₆·C₂₂H₂₈O₄N₂. C. A. R.

Remarks on Mr. M. Nierenstein's studies on catechol. KARL FRUENDENBERG *Ber.* 55B, 1938–42(1922).—Answer to the criticism of N. (*J. Chem. Soc.* 121, 604 (1922), and earlier papers).

C. A. R.

Dioximes. G. PONZIO. *Atti accad. sci. Torino* 57, 384(1922).—By the action of NH₂OH on BzC:(NOH)Ac P. obtains a mixt. of 2 dioximes, m. 135° and 194°, rather than one m. 178° as reported by previous investigators. They are 2 forms of methylbenzoylglyoxime, MeC:(NOH)C:(NOH)Bz, and P. undertakes to show that they can-

not be the *syn*-, *anti*-, *amphi*-, *ana*-forms of Hantzsch and Werner. P. limits himself to the reaction with N_2O_4 (abs.) (which is used in ether soln. at low temps., and which does not induce intramol. transpositions). The "*a*"-form, m. 135°, gives $MeC(:NOH)C(:N_2O_4)Bz$, the "*b*"-form, m. 194°, gives the peroxide $Me(C_2N_2O_4)Bz$. The formation of a ketopseudonitrol oxime shows unequivocally that the two NOH groups of the *a*-methylbenzoylglyoxime are not equiv., the formation of a peroxide shows that in *b*-methylbenzoylglyoxime the NOH groups are equiv., as each loses 1 atom of H. The behavior is best explained by assigning the tautomeric structures, nitroso-oxime and dioxime, $MeC(:NOH)CH(NO)Bz \rightleftharpoons MeC(:NOH)C(:NOH)Bz$, to the *a*- and *b*-form, resp. The *a*-nitroso-oxime shows how by action of N_2O_4 it can be transformed to $MeC(:NOH)C(NO)(NO_2)Bz$; it shows how the di-Ac deriv. is formed; and, by loss of a mol. of water, the furazan is formed, $MeC \text{---} CBz$. The *b*-methylbenzoylgly-



oxime form is in accord with the reactions shown by it, as the formation of a peroxide $Me(C_2N_2O_4)Bz$, of the di-Ac and di-Bz derivs. *b*-Methylbenzoylglyoxime reacts in H_2O with metallic Cu, Ni, Co, and Fe just as the *a*-salt which Chugaev considers as the *syn*-form. Both give methylphenyltriketone trioxime when treated with NH_4OH . This exists in 2 forms as it gives 2 series of derivs.; both react in H_2O with metallic Ni. *a*-Methylbenzoylglyoxime is best prepd. by treating alc. $BzC(:NOH)Ac$ with the theoretical quantity of $NH_4OH.HCl$ and $NaOAc$ in water, and heating to 60-70° several hrs. On dilg. an almost quant. yield is obtained. The product is washed and redissolved in 50% alc., a 20% excess of $Ni(OAc)_2$ is added, which ppts. the *b*-form. Then the *a*-form is pptd. with $Cu(OAc)_2$ from a soln. which has been made neutral by adding NH_4OH . H_2SO_4 is added to liberate the glyoxime, which is then extd. with ether, and dried over Na_2SO_4 . Then it is redissolved in anhyd. ether, agitated with bone black, filtered, and petroleum ether added till the soln. becomes turbid. White plates of the pure *a*-glyoxime are deposited on standing, m. 135° (decompn.), sol. in water, alc., ether, acetone, insol. in $PhMe$, $CHCl_3$, C_6H_6 , sol. in alkalies and concd. H_2SO_4 . The aq. soln. does not attack Ni or Co. Heated to 80-90° it loses a mol. of water to give methylbenzoylfurazan, $MeC \text{---} CBz$ whereas the *b*-glyoxime gives



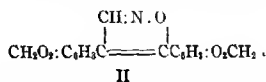
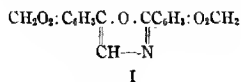
the anhydride only on heating with Ac_2O . Many solvents convert it to the *b*-form, but the reaction is never complete. *Copper salt*, $C_{10}H_9O_3N_2Cu$, is prepd. by treating the *a*-glyoxime in dil. alc. soln. with $Cu(OAc)_2$, and then neutralizing with NH_4OH , to drive the reaction to completion. Dried in a vacuum, it appears as an olive powder which, when heated rapidly, explodes at 185°; heated slowly, it m. about 195° (decompn.). It is insol. in the common org. solvents, sol. in NH_4OH and $NaOH$, easily decompd. by mineral acids giving the *a*-glyoxime. The *diacetyl derivative* appears together with methylbenzoylfurazan and a NO deriv., on dissolving the *a*-glyoxime in Ac_2O in the presence of fused $NaOAc$. This is poured into water and the soln. neutralized with Na_2CO_3 , when a greenish paste seps., which is washed with ether, in which it is slightly sol. It is recrystd. from alc. appearing as flattened white prisms, m. 113°, insol. in water, petroleum ether, sol. in C_6H_6 , $CHCl_3$, and acetone. Heated with water it gives methylbenzoylfurazan. *α -Oximino- β -pseudonitrol- γ -ketophenylbutane*, $MeC(:NOH)C(:N_2O_4)Bz$, is made by treating the *a*-methylbenzoylglyoxime in cold Et_2O with a mol. of N_2O_4 . The soln. is washed with water, dried over Na_2SO_4 , the ether partially distd. off, and then petroleum ether added, when the substance seps. as white prisms, m. 111° (lively decompn.), insol. in water, petroleum ether and ligroin, slightly sol. in C_6H_6 , and $CHCl_3$, sol. in acetone and alc. Exposed to the air, it is stable; but in a sealed tube it decomp. with evolution of nitrous fumes. *b*-Methylbenzoylglyoxime.—The Ni

salt obtained above is purified by recrystg. from C_6H_6 , then it is treated with 20% HCl in ether to liberate the glyoxime, which is then recrystd. from alc. Large prisms are obtained, m. $193-4^\circ$ (decompn.), insol. in C_6H_6 , $CHCl_3$, ligroin, slightly sol. in water and PhMe, very sol. in alc., ether, and acetone. In H_2O it slowly attacks Ni, Cu and Co. Treated with N_2O_4 it gives the anhydride; treated with NH_4OH , it gives the trioxime. *Nickel salt*, $(C_{10}H_9O_2N_2)_2Ni$, is made by treating *b*-glyoxime in alc. with $Ni(OAc)_2$. The reaction comes to an equil., but it can be driven nearly to completion by neutralizing with NH_4OH . From C_6H_6 it appears as blood-red needles, m. 258° , decomps. 260° , insol. in water and ligroin, slightly sol. in hot and less in cold C_6H_6 and $CHCl_3$, slightly sol. in acetone, alc., and ether. Mineral acids decomp. it; NaOH dissolves it slowly, and in time $Ni(OH)_2$ is pptd. The *a*- can be transformed to the *b*-form by boiling the *a*-form with $CHCl_3$ and heating the resulting crystals in H_2O in the presence of Ni; the *b*-glyoxime seps. and can be recrystd. from C_6H_6 . *Copper salt*, $(C_{10}H_9O_2N_2)_2Cu$, besides being formed by the reaction of the metal on the *b*-glyoxime, is prepd. by treating the glyoxime in AcOH with Cu, the compd. sepg. as a coffee-colored powder, m. 201° (decompn.), insol. in the common org. solvents, sol. in 20% NaOH, the Na salt of the *b*-glyoxime being present in soln. *Cobalt salt*, $(C_{10}H_9O_2N_2)_2Co$, seps. when the metal is acted on by *b*-glyoxime, and is prepd. by treating the glyoxime in AcOH with $Co(OAc)_2$. It does not m. up to 300° and easily gives colloidal solns. in many org. solvents, possibly even in NaOH, in which it dissolves slowly, giving a dark yellow-orange soln. The mineral acids decomp. it, but AcOH does not touch it even in boiling soln. The *diacetyl derivative* is obtained by treating in the cold *b*-methylbenzoylglyoxime with Ac_2O in the presence of NaOAc, and recrystg. from alc.; white prisms, m. 68° , but not becoming clear until heated to 100° , insol. in water, sol. in most org. solvents, excepting petroleum ether and ligroin. Exposed to the air it is stable. NaOH hydrolyzes it in the cold to the original glyoxime. *Dibenzoyl derivative*, $MeC(:NOBz)C(:NOBz)Bz$, is prepd. by treating the *b*-glyoxime in NaOH or C_6H_5N with $BzCl$, and recrystg. from $CHCl_3$; white prisms, m. $220-1^\circ$ (slight decompn.), slightly sol. in alc., acetone, and ether, sol. in $CHCl_3$ and C_6H_6 , insol. in water and ligroin, slowly hydrolyzed back to the glyoxime by boiling NaOH. In this way the *a*- may be transformed to the *b*-form. The *peroxide* $Me(C_2N_2O_2)Bz$ is made by treating the *b*-glyoxime in Et_2O with N_2O_4 , drying over Na_2SO_4 , and recrystg. from alc. It appears as long white needles, m. 70° , sol. in hot and slightly in cold alc., and in petroleum ether, sol. in the other org. solvents, insol. in water. Reduced with Zn dust and AcOH, it gives the original glyoxime. It does not react with ammonia even at 100° . *a-Trioxime of methylphenyltriketone*, $MeC(:NOH)C(:NOH)C(:NOH)Ph$ is made by heating on a water bath with $NH_4OH.HCl$ and NaOAc in dil. alc. soln.; recrystd. from water it appears as white prismatic needles, m. 201° (lively decompn.), sol. in alc., ether, acetone; slightly sol. in hot C_6H_6 , $CHCl_3$, ligroin, and water, very sol. in cold water. In H_2O it attacks Ni, Co, Cu, and Fe. *Nickel salt* $(C_{10}H_9O_2N_2)_2Ni$, results from the direct action of the *a*-trioxime and $Ni(OAc)_2$. It is a yellow-orange powder. Heated to 280° it changes without melting. It is insol. in water, slightly sol. in the org. solvents, sol. in 20% NaOH, and is decompd. by mineral acids. Cobaltous and copper salts may be obtained, as above. *Triacetyl derivative* is formed by acetylating the *a*-trioxime with Ac_2O in the presence of NaOAc, and recrystg. from ligroin, prisms, m. 111° , insol. in water, sol. in alc. and $CHCl_3$, very sol. in hot and slightly in cold C_6H_6 and acetone, almost insol. in ether. NaOH hydrolyzes it slowly to the trioxime. *b-Trioxime* is prepd. by treating *b*-methylbenzoylglyoxime in 30% NaOH, and adding slowly, with cooling, an excess of solid $NH_4OH.HCl$. After 12 hrs. it is dild. with water, neutralized with a current of CO_2 , and recrystd. from water; white needles melt 196° (decompn.)

if heated rapidly, and at a lower temp., if heated slowly, very sol. in hot, and slightly in cold water, sol. in alc., ether, acetone, insol. in C_6H_6 , $CHCl_3$, and ligroin, sol. in alkalis and ammonia, also in H_2SO_4 . In H_2O , it attacks Ni and Fe, but unlike the α -form, it does not touch Cu, or Co. However, it still gives ppts. with the salts of these metals, which have not been studied. *Nickel salt*, $(C_{10}H_{10}O_2N_2)_2Ni$, recrystd. from alc., appears as orange plates, m. 236° , insol. in water, quite sol. in hot, slightly in cold alc., slightly sol. in ether, $CHCl_3$, acetone, insol. in C_6H_6 and ligroin, sol. in NaOH, decompd. by mineral acids. *Triacetyl derivative*, $MeC(:NOAc)C(:NOAc)C(:NOAc)Ph$, is prepd. by acetylating the β -trioxime in the cold with Ac_2O , in the presence of fused NaOAc. It crystd. from alc. as large prisms, m. 107° , insol. in water, very sol. in hot, slightly in cold alc., slightly sol. in ligroin, and ether, sol. in acetone, $CHCl_3$, and C_6H_6 . A. W. C.

Isomerism of the oximes. X. Cinnam- and nitrocinnamaldoximes. O. L. BRADY AND C. D. THOMAS. *J. Chem. Soc.* 121, 2098-110(1922); cf. *C. A.* 14, 3639.—*Benzoylcinnam-anti-aldoxime*, prepd. from the mixed oximes and $BzCl$, long needles, m. 122° . This is probably the *syn*-deriv. described by Richter. Hydrolysis of this with 2 *N* NaOH at 100° is the most convenient method of prep. *cinnam-anti-aldoxime* (A), *Carbanilincinnam-anti-aldoxime*, from the *anti*-oxime and $PhCNO$, rectangular crystals, decomp. 138° . Hydrolysis with 2 *N* NaOH gave $PhNH_2$, $(PhNH)_2CO$ and A. The corresponding *syn*-oxime forms a bright yellow microcryst. powder, m. 76° . On boiling with alc., a colorless oxime is obtained, decomp. 84° . Both forms decomp. on standing and on hydrolysis with 2 *N* NaOH to yield $PhNH_2$, $(PhNH)_2CO$ and $PhCH:CHCN$. *Cinnam-anti-aldoxime 2,4-dinitrophenyl ether*, pale yellow powder, decomp. 188° . The *o*-benzyl ether forms rectangular plates, m. 88° . The *N*-benzyl ether from the *syn*-aldoxime (cf. *Ann.* 298, 192) forms pale yellow glistening plates, m. 180° . *m*-Nitrocinnam-anti-aldoxime, yellow, rectangular plates, m. 157° . The isomeric form could not be isolated from the mother liquor. *Acetate*, pale lemon-colored plates, m. 136° . Boiled with 5 parts Ac_2O for an hour, *m*-nitrocinnamionitrile results, pale yellow needles, m. 160° . *Carbanilino-m-nitrocinnam-anti-aldoxime*, pale yellow needles, m. 140° (decompn.). *o*-Nitrocinnam-anti-aldoxime, fawn-colored, pearly leaflets, m. 134° . *Acetate* m. 107° . *Carbanilino derivative*, bright yellow powder, m. 104° , decomp. below 110° . *p*-Nitrocinnam-anti-aldoxime (cf. *Ann.* 253, 349). *Acetate*, deep yellow octahedrons, m. 158° . *Carbanilino derivative*, yellow, m. 133° . *p*-Nitrocinnamionitrile, yellowish brown needles, m. 202° . C. J. WESS

Mechanism of the formation of benzoylbenzoin by treatment of benzoylmandelonitrile with an alcoholic solution of sodium ethoxide. HERBERT GREENE AND ROBERT ROBINSON. *J. Chem. Soc.* 121, 2182-96(1922).—The yield of $PhCOCHPhOBz$ is considerably increased when BzH is added to the reacting mixt. This favors the view that the necessary 1st step is the alcoholysis into $BzOEt$, a cyanide and BzH , which last undergoes condensation with a 2nd mol. of $PhCH(OBz)CN$ (A). *Benzoylpiperoin* (B), $CH_3O_2C_6H_4COCH(OBz)C_6H_4O_2CH_3$, from benzoylmethylenedioxymandelonitrile (C), piperonal and $EtONa$, diamond-shaped prisms, m. 169° . In 1 expt. on the prepn. of C, a compound was obtained, $C_{17}H_{11}O_5N$, thin, pale greenish yellow flakes, m. 153° . *2,5-Dipiperonyloxazole* (I), by the action of HCl upon piperonal and its cyanohydrin in Et_2O , needles, m. 213° . Solus. in C_6H_6 and $EtOH$ exhibit violet fluorescence. *Hydrochloride*, greenish yellow, hydrolyzed by H_2O or $EtOH$. HNO_3 gives a NO_2



deriv., canary-yellow needles. It may be that the above compd. is an *isoxazole* (II). Condensation of A and *p*-MeOC $_6$ H $_4$ CHO gave 4'-methoxybenzoylbenzoin, monoclinic

prisms, m. 119.5–20.5°. Piperonal and A gave 3',4'-methylenedioxybenzoylbenzoin, prisms or hexagonal tablets, m. 134–5°. 6'-Nitro derivative, pale yellow, dense aggregates of short prismatic needles, m. 172°. 3,4-Methylenedioxybenzoylbenzoin, $\text{PhCH}(\text{OBz})\text{COC}_6\text{H}_3\text{O}_2\text{CH}_3$, from C and BzH , small octahedrons from EtOH , m. 147.5–8.5°. This does not yield a NO_2 deriv. when treated with HNO_3 in AcOH . 6'-Nitropiperoin (D), by adding a mixt. of HNO_3 and AcOH to piperoin suspended in AcOH , hexagonal prismatic needles, changing in color from pale to intense yellow on standing, m. about 166° (decompn.). 6'-Nitro-3,4,3',4'-dimethylenetetraoxybenzoylbenzoin (nitrobenzoyl-piperoin) by adding HNO_3 - AcOH to benzoylpiperoin, in AcOH , slender, pale yellow needles, m. 160.5–1.5°. 6,6'-Dinitropiperoin (C), prepd. by the action of HNO_3 at 5° on piperoin, double fish-tail crystals from AcOH , decomp. 240°. A boiling PhNO_2 soln. of D or E finally deposits a brick-red acid substance, which HNO_3 converts into 6,6'-dinitro-3,4,3',4'-di[methylenedioxy]azobenzene (C. A. 10, 755). 6,6'-Dinitropiperil, by the nitration of piperil at 5°, golden yellow needles, decomp. above 200°. H_2O_2 in AcOH oxidizes it to 6-nitropiperonylic acid. Piperil and $\alpha\text{-C}_6\text{H}_4(\text{NH})_2$ give 2,3-dipiperonylquinoxaline, hexagonal tablets, yellow by reflected and green by transmitted light, m. 204°. The concd. H_2SO_4 soln. is indigo-blue and becomes red on diln. Homopiperonyl methyl ether, by the action of MeONa on the bromide, b_m 127°. 6-Nitro derivative, silky golden yellow needles, m. 114.5–5.5°. Methyl 6-nitropiperonylacetate, pale yellow needles, m. 105°. Benzoyl-3-benzoyloxy-4-methoxymandelonitrile, prepd. by shaking an ice-cold aq. soln. of vanillin, KOH and KCN with BzCl , octahedrons, m. 143–8°. A table of color reactions in concd. H_2SO_4 is given. C. J. Wzsr

Labile nature of the halogen atom in organic compounds. V. The action of hydrazine on the halogen derivatives of some esters and substituted cyclohexanes. E. L. HIRST and A. K. MACBETH. *J. Chem. Soc.* 121, 2169–78(1922); cf. C. A. 16, 2848.—The reaction of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ upon a further series of representative substances is discussed and additional evidence in favor of the view that halogen atoms susceptible to reduction are endowed with an induced electropositiveness and that their sp. chem. properties are connected with this factor. The 4-Cl, 4-Br, and 4,4-Cl₂ derivs. of 1,1-dimethylcyclohexane-3,5-dione do not react with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. The 4,4-Br₂ and the 4,4-ClBr derivs. each lose 1 atom of Br. Cyclohexanespiro-4-chloro- and -4-bromocyclohexane-3,5-dione did not react with N_2H_4 , but the 4,4-ClBr deriv. lost the Br atom. Succinchloro- and -bromoinimides react vigorously, as would be expected from the theory. 1-Chloropiperidine liberates 1 mol. N from N_2H_4 . The Br derivs. of acetyl- and diacetyl-succinate both react with N_2H_4 . $\text{CHCl}(\text{CO}_2\text{Me})_2$, $\text{CCl}_2(\text{CO}_2\text{Me})_2$, $\text{CBrCl}(\text{CO}_2\text{Et})_2$, and $\text{MeCCl}(\text{CO}_2\text{Et})_2$ as well as $\text{MeCBr}(\text{NO}_2)_2$ liberate 1 mol. N from N_2H_4 . $\text{CPrCl}(\text{CO}_2\text{Et})_2$ liberates less than 0.5 the vol. expected in 4 hrs. C. J. W.

Constitution of the terpene present in the essential oil from Andropogon jwarancusa, Jones. J. L. SIMONSEN. *J. Chem. Soc.* 121, 2292–9(1922); cf. C. A. 16, 419.—The new terpene previously mentioned as being present in the essential oil from *Andropogon jwarancusa*, Jones, is shown to be *d*- Δ^4 -carene, b_m 165.5–7°, d₂₀²⁵ 0.8552, n_D²⁰ 1.474, $[\alpha]_D^{20}$ 62.2°, $[\rho]_D^{20}$ 44.69. Oxidation with KMnO_4 in AcMe at 0° gave *d*-1,1-dimethyl-2- γ -ketobutylcyclopropane-3-carboxylic acid, $\text{AcCH}_2\text{CH}_2\text{CH}(\text{CM}_2\text{CH}_2\text{CO}_2\text{H})_2$, vis-

cous, pale yellow oil, purified through the semicarbazone, glistening rhombohedrons m. 182–3°. Sodium salt of the acid, prisms. Oxime, hexagonal prisms, m. 124–5°; $[\alpha]_D^{20}$ +44.9° in 2% MeOH . Phenylhydrazone, long yellow prisms, m. 97–9°. It is very unstable and decomps. overnight. Ethyl ester, b_m 133–5°; its semicarbazone forms rosetts of needles, m. 119–20°. The keto acid, on treatment with NaOBr , is converted quantit. into *d*-3-carboxy-1,1-dimethylcyclopropane-2-propionic acid, minute, irregular plates m. 104–5°, $[\alpha]_D^{20}$ 33.5° in 1% CHCl_3 . Copper salt, sparingly sol. The action of HBr on this acid gave homoterpenylic acid. The action of HCl on *d*- Δ^4 -carene gives

dipentene-HCl and sylvestrene-HCl. *Ethyl d-pinonate semicarbazone* m. 152-4°. The *l*-compound m. 152-4°. C. J. Wæst

Comparison of α -campholonic acid with Mahla-Tiemann's dihydrocampholenic acid and with isocampholic acid. P. Lapp. *Ber.* 55B, 1883-92(1922); cf. M. and T., *Ber.* 33, 1929(1900); van Kregten, *C. A.* 11, 1650.—*dl*- α -Campholenic acid (A), b_D^{20} 148.2-9.2°, was prepd. from *dl*-camphor oxime and purified through the NH₄ salt and the amide, m. 115-6°. With 0.1 part Pt sponge and H in Et₂O, A quant. gives in 1 hr. *dl*-*cis*- α -campholonic acid (B), b_D^{20} 150.9-1.2°, adds no Br in CHCl₃, is stable only a short time (1 min.) towards 5% alk. KMnO₄, d_4^{25} 0.9750, n_D^{25} 1.45973; *chloride*, prepd. with a 5% excess of PCl₅ in petr. ether, b_D^{20} 102-4°; *amide*, leaflets from C₆H₆, m. 129-30°; *anilide*, flat prismatic crystals from C₆H₅-petr. ether, m. 140-1°. B is also obtained in 70% yield by passing A and H over a Ni catalyst at 200°. Since the amide and anilide melt somewhat higher than the corresponding derivs. of M. and T.'s dihydrocampholenic acid (C), it was suspected that B and C might be stereoisomers. Skita's work (*C. A.* 15, 852) has shown that hydrogenation of double bonds in acid media gives chiefly *cis*-comps., while in alk. or neutral soln. the formation of *trans*-comps. seems to be favored. Now the amide of A in Et₂O-MeOH with Pt sponge and H gives after 12 hrs. *trans*- α -campholonic amide, leaflets, m. 124.5-5.0°, identical with that obtained from C prepd. by M. and T.'s method. Guerbet's isocampholic acid (D), which is obtained as a by-product, together with campholic acid (E) as the chief product, in the rupturing of the ring in camphor by alkalis, might be conceived as resulting from the rupturing of the ring between C atoms 1 and 2 (E resulting from a more rapid rupturing between C atoms 2 and 3), in which case it would be identical with C, as believed by M. and T., although they had no exptl. proof for their belief. *dl*-D was accordingly prepd. essentially by G.'s method and was found not to be identical with C; it is an almost odorless oil, b_D^{20} 140-2°, stable towards Br in CHCl₃; cond. measurements on its Na salt and on that of *dl*-E showed that, contrary to the general belief, D is not a much stronger acid than E, the dissociation of its Na salt ranging from 82% for V 32 to 94% for V 1024 and that of the salt of E from 75 to 93% for the same concns.; the Na salt of D in H₂O is decompd. by CO₂ almost as easily as that of E. D therefore seems to be a secondary product formed from E by a steric rearrangement under the influence of the alkali. *Chloride*, b_D^{20} 88-9°. *Amide*, long pointed flat prisms from H₂O, m. 109-10°. *Anilide*, m. 137-9°. C. A. R.

Ketonanils. E. KNÖVENAGEL. II. Constitution of the *N*-alkylketonanils and conversion of aliphatic ketonanils into quinoline derivatives. HANS BÄHR. *Ber.* 55B, 1912-28(1922); cf. *C. A.* 16, 252.—Indirect and direct evidence is given that of the 2 structures, Me(CH₂)₃CNPhCH₂R (A) and Me₃C.NPh.CHR (B), suggested in the first

paper for the "*N*-alkylketonanils" (C) resulting from the cleavage with alkali of the ketonanil alkiodides A is the correct one. The indirect evidence is that the methiodides of comps. of the type RN:CHR' and RN:CR', where R and R' are aromatic residues, do not yield derivs. of a 3-membered ring analogous to B on cleavage with alkali or dry distn. *in vacuo*. Attempts to det. the structure directly by means of the v. Bayer and Caro cleavage of nitrosodialkylanils by alkalis (R₂NC₆H₄NO + NaOH = RNHR + NaOC₆H₄NO) failed; the action of the HNO₃ followed a different course (it probably added at the double bond of the aliphatic residue in the C) and the intended cleavage with alkali could not be carried out. That A is the correct structure is shown unequivocally, however, by the fact that the ethiodide of "methylacetone-*p*-tolil" (D) and the methiodide of "ethylacetone-*p*-tolil" (E) are identical, which is conceivable only if D and E have structures of the type A. This conception of the C as being simply unsatd. dialkylanils explains all their reactions. There are many reactions analogous to the formation of the C, as, e. g., the action of alkalis on the alkiodides of pyridine, quinoline,

isoquinoline and mesidine derivs., resulting in their conversion into ammonium bases which are capable of a rearrangement with a simultaneous decrease in the valence of the N (cf. Vongerichten and Rotta, *C. A.* 5, 3063). $\text{Me}_2\text{C:NPh}$ (F) was prepd. as described in the first paper, except that the time of boiling was reduced to 10 hrs.; it generally yielded a glassy methiodide which with NaOH gave the same *isopropenylmethyl-aniline* (G) (the "methylacetonanil" of the first paper) as the cryst. methiodide, but, in addn., about 15% of a base $\text{C}_{22}\text{H}_{30}\text{N}_2$, stout needles from AcOEt , m. 147° , mol. wt. in freezing C_6H_6 303-8. Slowly brought together in Et_2O F and Me_2SO form an *addition product*, $\text{C}_{11}\text{H}_{17}\text{O}_4\text{NS}$, silvery leaves from alc., m. 148° , gives with NaOH in H_2O 88.7% G, b₁₄ 144° . With NaNO_2 10 g. G in dil. HCl gives 6 g. of a ppt., difficultly crystd. from alc., m. $85-91^\circ$. *Diiodide* of G, from G and I boiled a few min. in alc., m. $138-40^\circ$, yields a light yellow oil on heating with alkalis. *Benzophenonanil methiodide* (H), from 5 g. of the anil, 2.8 g. MeI and 0.5 g. ligroin heated 6 hrs. at 120° in a sealed tube, yellowish white needles from C_6H_6 , m. 120° , is decompd. by dil. NaOH, even in the cold, according to the equation $\text{PhNMeI:CPh}_2 + \text{H}_2\text{O} = \text{PhNH}_2\text{HI} + \text{Ph}_2\text{CO} + \text{MeOH}$. *Benzophenone-p-tolil methiodide* (I), from the components heated 8 hrs. at 100° in a sealed tube, m. 198° ; if, in crystg. it from MeOH, the soln. is boiled a few min. there sep. on long standing the prismatic columns of $\text{Ph}_2\text{C(OMe)}_2$, m. 107° ; heating with H_2O hydrolyzes the methiodide to Ph_2CO and $\text{MeC}_6\text{H}_4\text{NH}_2$. F. MeI slowly heated under 14 mm. splits off HI at about 135° and gives 47.5% G; H under 18 mm. yields traces of PhNH_2 at 93° and a few drops of Ph_2CO at 170° , the temp. then rising slowly to above 250° without further cleavage and the original H, partly resinsified, remaining in the distg. flask; I behaves in the same way. *N-Benzylidene-p-toluidine methiodide*, from the components allowed to stand together 24 hrs., when heated under 14 mm. gives a couple drops of $\text{MeC}_6\text{H}_4\text{NH}_2$ at 100° and the rest resinifies. *Isopropenylmethyl-p-toluidine ethiodide*, obtained in small yield from D after a long time, is identical with *isopropenylethyl-p-toluidine methiodide*, quite easily obtained from 1 mol. each of E and MeI; it seps. from alc. in light yellow needles, m. 246° . With 1 mol. PCl_5 G yields a dark blue dye sol. in alc. with dark blue color, reprecip. by H_2O in blue flocks, sol. in concd. acids with dark brown-red color, reprecip. by alkalis, sol. in alc. alkalis with the same color as in acids, dyes wool a beautiful dark blue; as it is also obtained by treating G successively with COCl_2 and POCl_3 it probably has a structure corresponding to that of parafuchsine. From 30 g. G treated at $180-200^\circ$ with dry HCl are obtained CH_4 , MeCl, PhNH_2 and 16.3 g. 2,4-dimethylquinoline (J), b₁₅ 143° ; *picrate*, m. 194° ; *tartrate*, m. 158° , loses CO_2 10° above the nt. p.; methiodide, m. 211° , gives with alkalis a yellow oil quickly altering with formation of cyanine-like dyes but if it is at once taken up in Et_2O it gives with aq. tartaric acid a salt m. 148° with 4.38-4.47% N. J can likewise be obtained from F, the reaction doubtless proceeding, like the rearrangement of PhN:CHMe into quinaldine (v. Müller and Plöchl, *Ber.* 27, 1298(1894)), according to the scheme $2\text{G} \longrightarrow \text{PhNHCMe}_2\text{CH}_2\text{CMe:NPh} \longrightarrow \text{PhNHCM}_2\text{CH:CMeNHPh} \longrightarrow \text{J} + \text{PhNH}_2 + \text{CH}_4$. This reaction is quite general for the ketonanils and the C and can be effected under a great variety of conditions (with HCl gas at 180° , in sealed tubes at $250-300^\circ$, with AlCl_3 , ZnCl_2 , other halogen acids at the b. p.). Under the same conditions as in the prepn. of J, *p-MeC}_6\text{H}_4\text{N:CMe}_2 gives 2,4,6-trimethylquinoline (K), b_{12.5} $146-8^\circ$; *hydrochloride*, turns brown 245° , m. $268-72^\circ$; *tartrate*, m. 172° ; methiodide, stout light yellow needles from alc., m. $245-7^\circ$ (Pfitzinger, *J. prakt. Chem.* 38, 40(1888), gives $225-6^\circ$). $\text{Me(CH}_2)_2\text{CNMeC}_6\text{H}_4\text{Me}$ similarly gives K, CH_4 , MeCl and $\text{MeC}_6\text{H}_4\text{NH}_2$. MeEtC:NPh yields 92% 4-ethyl-2-methylquinoline (L), b₁₄ $150-3^\circ$; methiodide, m. 246° ; *tartrate*, needles from alc., m. 149° . The gases evolved in the formation of L consist of 70-80% C_2H_6 and 30-20% CH_4 . L is oxidized in boiling dil. H_2SO_4 by $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ to 2-methylquinoline-4-carboxylic acid, m. 244° . *p-MeC}_6\text{H}_4\text{N:}**

N:CMcEt in the same way gives *4-ethyl-2,6-dimethylquinoline*, b_{10} 169–71°; *tartrate*, m. 173°. III. Aliphatic-aromatic ketonanis. OSKAR GOOS. *Ibid* 1929–37.—*Acetophenonanil* (A) and *desoxybenzoinanil* (B) cannot be obtained by direct condensation of the ketones with PhNH_2 ; MeCOPh and PhNH_2 heated with I always give 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$ and PhCH_2COPh remains unchanged. These compds. can be prepd., however, by heating the acetals of the ketones with PhNH_2 at the b. p. Unlike the purely aliphatic ketonanis, the aliphatic-aromatic compds. show but slight stability towards alkalis and acids. Even on gentle warming with H_2O , decompn. occurs. Like the aliphatic compds., however, they can be converted into quinoline derivs. by the methods described in the preceding abstr. A, obtained in 82% yield (together with 15–20% dypnonanil (C)) from 1 mol. each of $\text{PhMeC}(\text{OEt})_2$ and PhNH_2 refluxed 45 min., m. 41°, b_{11} 170° (in the presence of 1% of I the reaction takes place after 15–20 min. boiling), is light yellow when fresh, quickly darkens and gradually deliquesces in the air, is stable in sealed tubes, dissolves in 2–3 parts dil. HCl but decomp. in a few min. into PhCOMe and PhNH_2 ; with dry HCl in Et_2O , however, it gives the *hydrochloride* of A, flocculent ppt., m. 190°. Refluxed alone 20–30 min., A yields C which, heated another 30–45 min. near its b. p., gives 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$. *Methiodide* of A, from 1 mol. each of the components at room temp., slender rhomb-like crystals from alc. or alc.-ligroin, m. 209°. *Dimethyl sulfate addition product* of A, obtained in 70% yield from 1 mol. each of A and Me_2SO_4 in Et_2O , m. 159°; this or the methiodide with dil. NaOH or Na_2CO_3 decomp. into PhCOMe, PhNH_2 , MeOH and H_2SO_4 or HI. With dry HCl at 180–90° A. HCl gives C_6H_5 , PhNH_2 , 2-methyl-4-phenylquinoline and 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$. *Desoxybenzoin-acetal* (40 g. from 30 g. of the ketone, 24 g. $\text{HC}(\text{OEt})_2$ in 23 g. of 95% alc. and 0.1% concd. HCl allowed to react 22 hrs.), refractive oil, b_{14} 172°; boiled 0.5 hr. with 1 mol. PhNH_2 it gives 91% B (α -form), very slender light yellow prisms, m. 74°, sol. in concd. H_2SO_4 with deep emerald-green color, deliquesces in the presence of moisture with formation of PhCH_2COPh and PhNH_2 , oxidizes in the air in 18 hrs. to α -benzilanil (D), m. 96°. The B is isomeric with Busch and Falco's compd. (β -form) obtained from $\text{PhC}(\text{NCl})\text{NHPh}$ and PhCH_2MgCl (C. A. 4, 3237), m. 88°, into which the α -form rearranges when refluxed 45–60 min. under 14 mm. (218°). The α -B is decompd. by dil. HCl at 40–50° into PhCH_2COPh and PhNH_2 but in dry Et_2O with HCl it yields the *hydrochloride* as a light yellow finely cryst. ppt. m. 178–9°, stable in the air when dry. *Dimethyl sulfate addition product* of α -B, m. 139°. α -D, as had already been observed (K. and Moses, C. A. 8, 2156) rearranges on long standing into β -D, m. 105°. In concd. soln. the D decomp. according to the equation $\text{D} + \text{O}_2 = \text{PhCOCPhN:Ph} + \text{H}_2\text{O} = \text{PhCONHPh} + \text{PhCHO}$, the β - apparently giving about twice as much BzNHPh as the α -D.

C. A. R.

The Friedel and Crafts reaction with phthalic anhydride. T. C. McMULLEN. *J. Am. Chem. Soc.* 44, 2055–60 (1922); cf. Lawrence and Oddy, C. A. 16, 1573.—The stages in the reaction between $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$, C_6H_6 and AlCl_3 may be represented thus: $\text{C}_6\text{H}_4(\text{CO})_2\text{O} + \text{C}_6\text{H}_6 + \text{AlCl}_3 \longrightarrow \text{clear soln.} \longrightarrow \text{viscous ppt.} \longrightarrow \text{o-BzC}_6\text{H}_4\text{CO}_2\text{H}$ (A). Various expts. have been carried out with these intermediate products. The "clear soln." resulting by shaking 5 g. $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$, 9 g. AlCl_3 and 20 cc. C_6H_6 about 30 min. at 10° gives when heated 2 hrs. with C_{10}H_8 80% A, 35% naphthoylbenzoic acids (B) and 5% naphthylphenylphthalide (C). The "clear soln." dild. with an equal vol. of Et_2O and allowed to stand 30 min. yields a heavy light brown oil which with dil. HCl gives only A, *in vacuo* over H_2SO_4 loses C_6H_6 , Et_2O and HCl and changes to a solid apparently identical with the "viscous ppt." above, and on the H_2O bath with C_{10}H_8 in C_6H_6 gives no B; the oil contains 2 atoms Al to 4.75 atoms Cl. These results suggest that the "clear soln." may represent 2 stages of the reaction and that only the 1st product will react with C_{10}H_8 to give B while only the 2nd product is pptd. by Et_2O . The

"viscous ppt.," prepd. by shaking 5 g. $C_6H_4(CO)_2O$, 9 g. $AlCl_3$ and 80 cc. C_6H_6 30 min., boiling 2 hrs. and drying at 75° , had an Al:Cl ratio of 0.322; calcd. for $C_{14}H_8O_2Al_3Cl_3$ 0.304. Heated 20 min. at 100° with 20 cc. PhMe and 3.75 g. Ac_2O it gives 0.14 g. A and 7.3 g. *p*-tolylphenylphthalide (D), m. 106° . The solid intermediate product from $C_6H_4(CO)_2O$, $AlCl_3$ and PhMe similarly treated with C_6H_6 and Ac_2O gives *p*-Me C_6H_4 -COC $_6H_4$ CO $_2$ H almost exclusively and only very little D. With $C_{10}H_8$ and Ac_2O the solid intermediate product from 20 g. $C_6H_4(CO)_2O$, 36 g. $AlCl_3$ and 80 cc. C_6H_6 gives 5 g. A, 3.5 g. α -naphthylphenylphthalide (E), m. $227-8^\circ$, and 20 g. of the β -isomer (F), m. $153-4^\circ$. These phthalides were also prepd. by the action of C_6H_6 and $AlCl_3$ on the acetyl derivatives, m. 141° and 140° , of α - and β - $C_{10}H_7$ COC $_6H_4$ CO $_2$ H, resp. The intermediate product from $C_6H_4(CO)_2O$, $AlCl_3$ and $C_{10}H_8$ apparently undergoes some reaction with C_6H_6 and Ac_2O but no phthalide could be sepd. from the gummy mass. The intermediate product from 10 g. $C_6H_4(CO)_2O$, $AlCl_3$ and C_6H_6 heated 15 min. with 15 g. anthracene and 7.5 cc. Ac_2O in 140 cc. C_6H_6 gives 6 g. A, 0.3 g. of a yellowish white cryst. solid, m. $171-3^\circ$, 1 g. of a brownish white cryst. solid, m. $280-3^\circ$ (these last 2 are probably anthrylphenylphthalides), and 10 g. of a non-cryst. gum. *o*-[α -Naphthylphenylmethyl]benzoic acid, from E in aq. alc. KOH boiled 16 hrs. with Zn dust, m. 189° ; the Ba salt, mixed with Ba(OH) $_2$ and slowly heated to 210° *in vacuo*, yields α - $C_{10}H_7$ -CHPh $_2$, m. 152° . β -Isomer (21 g. from 22 g. F), seps. from C_6H_6 in solvated crystals m. $76-7^\circ$ and, solvent-free, 150° ; 11 g. of the Ba salt at about 225° gives 7 g. β -naphthylidiphenylmethane, m. $73-4^\circ$.

C. A. R.

Occurrence of free radicals in chemical reactions. The radicals of the basic triphenylmethane dyes. HEINRICH WIELAND, EGON POPPER AND HERMANN SEFRIEN. *Ber.* 55B, 1816-34(1922); cf. *C. A.* 9, 2539.—The question was raised in the earlier paper whether simple org. reactions, such as the Wurtz synthesis, whose formulation would seem to necessitate the assumption of the intermediate formation of free radicals, might not proceed through satd. intermediate products which undergo rearrangements within the zones of union without dissociation, as in the benzidine rearrangement. That such is the case in the rearrangement of aromatic nitrosamines into *p*-NO compds. was shown experimentally; if the rearrangement of Ph $_2$ NNO were preceded by a dissociation into the radicals Ph $_2$ N and NO, these 2 radicals should also combine to PhNHC $_6H_4$ NO but as a matter of fact they yield Ph $_2$ NNO, exclusively. Another group of reactions has now been studied from this point of view, *viz.*, the decompn. of labile azo compds. Gomberg, by decompg. Ph $_2$ CN:NPh (A) at its m. p., obtained 2% Ph $_2$ CPh (*Ber.* 36, 1088(1903)). The observation that A decomps. into N_2 + 2Ph $_2$ C (*C. A.* 3, 2943) is no proof that the radical is formed directly in the reaction, for it might be produced secondarily from Ph $_2$ CCPh $_2$. It is conceivable that the reaction might proceed according to the scheme



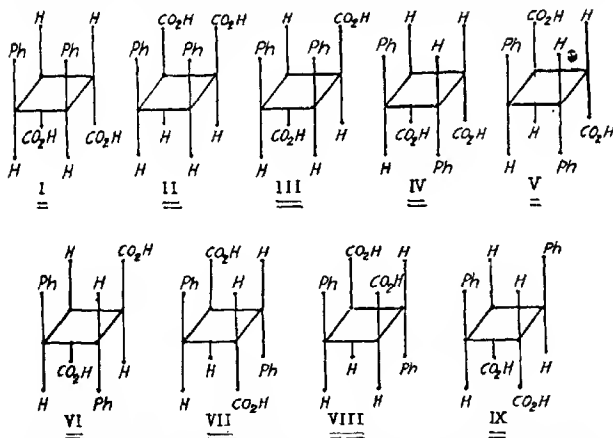
or groups set free for an instant from their unions being held by a kind of gravitation in the field of forc \acute{e} of the mol. until, being prevented from escaping as free radicals, they have again found a firm union at the free valences. The decompn. of A and its derivs. was studied, not by heating the solid compds. to their m. p., as done by Gomberg, but in solvents, it having been found that the liberation of N_2 is quant. at about 80° . In all the decompns. Ph $_2$ C was identified as one of the products by its spectrum, the deepening of the color on cooling and the formation of the peroxide with air or O. The max. yield was 35%. These results speak unequivocally for the view that the reaction proceeds according to the scheme $A \rightarrow N_2 + Ph_2C + Ph$. It might have been expected that the other radical, Ph, would be recovered as Ph $_2$, but no trace of this compd. was found; instead, the Ph was recovered as C_6H_6 . This result shows that the free valences of intermediate radicals need not necessarily be neutralized by mutual satn., *i. e.*,

by polymerization; the neutralization occurring in this case, which will be studied further, is analogous to the fate of HO ions set free at the anode, which do not give HO.OH but $\text{H}_2\text{O} + \text{O}$. The carbinols of malachite green and crystal violet and *p*-rosaniline with PhNHNH_2 yield the phenylhydrazo compds. $\text{R}_2\text{CNHNHPh}$, which are oxidized by Ag_2O to the corresponding azo compds. and these decomp. like A into the free radicals of the dyes, which, strange to say, are no more or only slightly more deeply colored than Ph_3C itself; their hot solns. (90°) are dark orange-red, becoming yellow with an orange tinge on cooling; they are decolorized by shaking with air; the peroxides, like the radicals themselves, are unstable, sepg. in colorless flocks which soon resinify; the spectra of the radicals show characteristic bands. The unexpected lack of influence of the basic groups on the absorption of these radicals is another example of the difficulties not infrequently met with in attempting to correlate constitution and color. It is felt, however, that the above results confirm the validity of the quinonoid structure for the Ph_3CH dyes; they seem to exclude any kind of satn. of the radicals by salt formation at the methyl C atom, for according to the present results there is a weakening rather than an increase of the absorption. A was prepd. by treating Ph_3CCl with PhNHNH_2 and, without isolating the hydrazo compd., treating the Et_2O soln. of the product, after removing the $\text{PhNHNH}_2\cdot\text{HCl}$, directly with Br water. For the decompn. of the A was used a sample of Kahlbaum ligroin which was purified by shaking 1 day with concd. H_2SO_4 (renewed several times), washing with H_2O , shaking several hrs. with satd. KMnO_4 (also renewed several times) until there was no further reaction, shaken several hrs. with HNO_3 , and treated with Sn and concd. HCl to remove any NO_2 compds. which might have been formed. All the decompns. were carried out in dry N (passed over heated Cu and through H_2SO_4). Besides Ph_3C there were obtained Ph_3CH and a little CPh_4 , and C_6H_6 was identified, after nitration, as PhNO_2 (isolated as $\text{PhNH}_2\cdot\text{HCl}$ after reduction with Sn and HCl) and $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$; in an expt. in which 0.092 g. C_6H_6 was obtained, the $(\text{Ph}_3\text{C})_2\text{O}_2$ isolated weighed 0.250 g., which corresponds to only 0.078 g. C_6H_6 ; there is much evidence which indicates that the Ph_3C first formed undergoes further changes during the reaction. Expts. are now under way to det. whence the radical Ph secures the H necessary for its conversion into C_6H_6 . *p*- $\text{ClC}_6\text{H}_4\text{NHNH}_2$, long needles, m. 85° , is obtained in stable form and in 85% yield by diazotizing *p*- $\text{ClC}_6\text{H}_4\text{NH}_2$ in HCl , slowly pouring the soln. into cold aq. Na_2SO_4 , letting stand a short time at room temp., heating to 70° , adding HCl , AcOH and Zn dust, concg. the now colorless soln., adding HCl , cooling, draining off the $\text{ClC}_6\text{H}_4\text{NHNH}_2\cdot\text{HCl}$, decomp. in H_2O with concd. NaOH , quickly drying the ppt. in a desiccator and subliming it *in vacuo*. $\text{Ph}_3\text{CNHNHC}_6\text{H}_4\text{Cl}$ m. $143\text{--}9^\circ$ (Gomberg and Campbell, *J. Am. Chem. Soc.* 20, 780, give 145°); the azo compd. m. 105° (C. and C., 103.5°). The decompn. of the latter in ligroin at 80° gives Ph_3C and PhCl (identified through its nitration products). [*p*-Chlorophenylazo]tri-*p*-tolylmethane (obtained in 70% yield from $(p\text{-MeC}_6\text{H}_4)_3\text{CCl}$ and 2 mols. *p*- $\text{ClC}_6\text{H}_4\text{NHNH}_2$ refluxed several hrs. in Et_2O , filtered and treated with the necessary amt. of Br water), intensely yellow crystals from C_6H_6 -gasoline, decomp. 116° ; its decompn. yields $(p\text{-MeC}_6\text{H}_4)_3\text{C}$. $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}:\text{NCPH}_2$ is the most stable of the azo compds. studied; it can be recrystd. from the ligroin used in the above expts. and its decompn. was therefore carried out in xylene at about 90° , giving Ph_3C and PhNO_2 (identified as PhNH_2). [Phenylhydrazo]tri-*p*-anisylmethane, prisms, m. 154° , converted by dry Ag_2O in C_6H_6 into the azo compound, yellow prisms from $\text{C}_6\text{H}_6\text{-EtOH}$, m. 106° (decompn.). [Phenylhydrazo]bis-*p*-dimethylaminotriphenylmethane, from the carbinol of malachite green refluxed 20 min. in satd. alc. soln. with PhNHNH_2 , crystals from $\text{CHCl}_3\text{-EtOH}$, m. 170° (decompn.), very sensitive towards acids; azo compound, golden yellow cryst. powder from $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$, m. 120° (decompn.), decomp. in ligroin at 80° like A. *p*-Chlorophenylhydrazo compound, crystals from $\text{C}_6\text{H}_6\text{-EtOH}$,

m. 124.5°; *azo compound*, fine golden yellow needles from Et_2O -gasoline, decomp. 116°. *Phenylhydrazotris-[p-dimethylaminophenyl]methane*, from the carbinol of crystal violet and PhNHNH_2 heated 30 min. at 100°, felted needles from CHCl_3 - EtOH , m. 172° (decomp.); *azo compound*, m. 150° (decomp.). *p-Chlorophenylhydrazo compound*, from the carbinol and $\text{ClC}_6\text{H}_4\text{NHNH}_2$ refluxed 20 min. in alc., crystals from C_6H_6 - EtOH , m. 178° (decomp.); *azo compound*, golden yellow prisms, decomp. 142°. *Phenylhydrazotris-[p-aminophenyl]methane*, from *p*-rosaniline heated 1.5 hrs. with PhNHNH_2 at 110°, needles from alc., m. 200°; converted by Ag_2O in cold Me_2CO into the *azo compound*, golden yellow needles from C_6H_6 , m. 195° (decomp.), decomp. only in high boiling ligroin at about 135° and the resulting dark brown soln. no longer gives the characteristic reactions of radicals. *p-Chlorophenylhydrazotris-[p-aminophenyl]methane*, from *p*-rosaniline and $\text{ClC}_6\text{H}_4\text{NHNH}_2$ heated up to 140°, leaflets from alc., m. 204° (decomp.), can be oxidized to the *azo compd.* only in $\text{C}_6\text{H}_5\text{N}$, not in Me_2CO .

C. A. R.

Configuration of the truxinic and truxillic acids. VI. R. STOERMER and F. BACHER. *Ber.* 55B, 1860-82(1922); cf. *C. A.* 15, 1888; de Jong, *C. A.* 16, 2683.—The question as to which of the 6 theoretically possible configurations (I-VI) of the truxinic acids (A) corresponds to each of the 4 known isomers had been settled definitely, and without having recourse to reactions which may proceed in 2 ways and whose mechanism is therefore not known, only for the β -A which, as a *cis*-dicarboxylic acid resolvable into active optical antipodes, can have only the configuration IV. β -A, the other known *cis*-dicarboxylic acid, must then have the configuration I or II; the reasons why it is probably



I have already been given. I and II are *meso*-forms and all attempts to resolve β -A into active components by means of cinchonine have failed; as such negative results have no great value as proofs, however, expts. are now under way to resolve the monoesters or monoamides of the acid into active components and to hydrolyze these back to the inactive form. δ - and neo-A are easily resolved into active components, which characterizes them beyond doubt as *trans*-dicarboxylic acids, in harmony with the fact that neither of them can form an anhydride or imide of its own. The δ -A on anhydridization goes over into the β -A and its NH_2 salt on dry distn. forms the imide of the latter

acid; as there is no migration of the Ph residues in these reactions, they must occupy the same (*trans*) positions in the 2 acids and δ -A must therefore have the configuration V or VI. The neo- bears to the β -A the same relation that the δ - does to the ζ -A and must therefore have the configuration III. The same close relationship between the 2 pairs of acids is shown by the fact that the ζ - is almost quant. rearranged into the δ -A by bases such as C_6H_5N or by HCl under pressure while the β - gives the neo-A. The formation of *trans*- from *cis*-dicarboxylic acids was already known but that *cis*- can be obtained from *trans*-acids seems less plausible at first sight. Apparently, in the truxinic and truxillic acid series, more than 2 large groups on 1 side of the plane of a ring are unstable towards hot HCl and a 3rd or 4th such group will migrate to the other side. As III gives I and not V or VI under such conditions it appears that the CO_2H migrate more easily than the Ph groups. Since, just as with I, no truxone has been obtained from the δ -A, the latter probably has the configuration VI rather than V; in VI, moreover, the light and heavy groups are most equally balanced and this configuration appears to be the most stable; as a matter of fact all the known A pass into δ -A on fusion with KOH. de Jong's method of detg. the configurations of the A (based on their formation from the cinnamic acids by polymerization under the influence of light) is criticized as being unreliable, for in the polymerization there may occur both *cis*- and *trans*-addn. of the 2 cinnamic acid mols. It had never been possible to obtain more than 10-4% of neo-A by heating the β -A with C_6H_5N in a sealed tube or with $PhNMe_2$ in an open vessel. It has now been found that heating with concd. NH_4OH gives a 20% yield but that the increased yield has no connection with the strength of the base is shown by the fact that 50% aq. NMe_3 does not further increase the yield. It was observed, however, in detg. the m. p. of β -A that there is always strong foaming immediately after fusion, and the anhydride of β -A can be isolated from the melt, but at the same time a CO_2H migrates and about 20% of neo-A is formed. As the formation of the latter therefore seems to depend merely on the influence of high temps., β -A was heated with H_2O alone under pressure and a 24% yield of neo-A was obtained. There is apparently no true equil.; at least it could not be shown definitely that neo- can be converted into β -A by merely heating with H_2O at 215° , although the transformation can be effected with HCl. Neo-A, unlike the ζ -acid, must be considered as a pseudoracemic conglomerate, for when the *d*-form is added to a satd. AcOH soln. of the inactive form there occurs neither soln. of the added acid nor a change in rotation of the filtered soln. de Jong's detns. of the configurations of the truxillic acids (B) are subject to the same criticism as in the case of the truxinic acids, but Stoermer's method, based on the resolution into optically active components, is likewise not applicable to the B for all 5 of the theoretically possible B are identical with their mirror images and can therefore not be resolved into optical antipodes. But by converting 1 of the CO_2H groups into CO_2Et , $CONH_2$, $CONHPh$, etc., the relatively asym. C atoms partially become truly asym. and of the resulting monobasic acids 2 are *dl*- and 3 are *meso*-forms. It has been found that α - and γ -truxillanillic acids are, as a matter of fact, resolvable into active forms and therefore α - and γ -B must have the configurations VII and VIII, and there can be no doubt that the γ -B, which forms a stable anhydride of its own, must have the configuration VIII. Esters of ϵ -B give with $PhMgBr$ a ditertiary alc., $Ph_2C(OH)C_6H_4Ph_2C(OH)Ph$, easily converted by dehydrating agents into a cryst. oxide and by HBr into a dibromide which can also be obtained from the oxide with HBr, a behavior entirely analogous to that of *cis*-terpinol and cineole, whence, in spite of the formation of ϵ - from α -B by fusion with KOH and the impossibility of obtaining a cryst. anhydride of ϵ -B or of reconverting it into α -B with concd. HCl in a sealed tube it may be concluded that ϵ -B is a *cis*-acid and has the configuration IX, but S. and B. will not commit themselves definitely to this view until they have completed further investigations now under way. A section

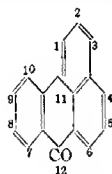
of the paper is devoted to a defense by Stoermer against the criticisms by de Jong of S.'s changes in the nomenclature of these acids. Neo-A is best prepd. by heating β -B 15–20 min. at 215° , powdering the cooled melt, digesting for a long time with Na_2CO_3 to sapon. the β -A anhydride, pptg. with HCl and sepg. the 2 acids as previously described by means of 5% alc. Of the neo-A 2.1835 g. dissolve in 100 g. AcOH at 20° , fused with 8 parts KOH, it rearranges quant. into δ -A while on heating with Ac_2O at 160° it regenerates β -A, which can be identified by evapg. the Ac_2O , taking up the residue in C_6H_6 , pptg. most of the neo-A with a little petr. ether, again evapg., boiling the residue a short time with concd. NH_4OH and pptg. the resulting β -truxinamic acid as the Na salt with not too dil. Na_2CO_3 . *Neotruxinyl chloride*, from the acid and SOCl_2 in C_6H_6 , crystals from C_6H_6 -ligroin, m. $83\text{--}4^\circ$, very unstable in the air, gives with 4 mols. PhNH_2 in C_6H_6 the *dianilide*, crystals from AcOH, m. $226\text{--}7^\circ$. When 2.5 g. of the acid in 42 cc. alc. is boiled with 2.5 g. cinchonine, the *salt* of the *d*-acid, m. $216\text{--}7^\circ$, at once seps. on cooling; the *d*-acid obtained from it, fine needles from alc., m. $236\text{--}7^\circ$, $[\alpha]_D^{18} 52.63^\circ$ (all detns. of $[\alpha]$ were made in Me_2CO); the *l*-acid, obtained from the mother liquors, m. $263\text{--}7^\circ$, $[\alpha]_D^{18} -52.87^\circ$, can also be obtained very pure ($[\alpha]_D^{20} -53.95^\circ$) through the *quinine salt*, felted crystals from alc., m. 138° . *d*-Neotruxinyl chloride, druses from C_6H_6 -petr. ether, m. $103\text{--}4^\circ$, $[\alpha]_D^{18} -15.98^\circ$; *dianilide*, scales from AcOH, m. $226\text{--}7^\circ$, $[\alpha]_D^{18} -53.23^\circ$; *amide*, m. $260\text{--}1^\circ$; *ethyl ester*, from the acid in alc. with HCl, fine needles from alc., m. 53° , $\alpha 0.370^\circ$ (0.2018 g. in 100 cc. Me_2CO in a 1-dm. tube); *methyl ester*, from the acid in Na_2CO_3 with Me_2SO , m. 100° , $[\alpha]_D^{20} 48.11^\circ$. *Methyl ester* of the *l*-acid, m. $100\text{--}1^\circ$, $[\alpha]_D^{20} -51.99^\circ$; *ethylamide*, from the chloride and 33% EtNH_2 , radiating bundles from dil. alc., m. 175° , $[\alpha]_D^{18} 30.30^\circ$; *methylamide*, fine felted needles from MeOH, m. $126\text{--}7^\circ$. *Cinchonine l*- δ -truxinate (3 g. from 3 g. *dl*- δ -A and 6 g. cinchonine in 50 cc. boiling alc. subsequently treated with 22 cc. H_2O), m. 192° ; free *l*-acid, long hair-fine needles, m. $158\text{--}9^\circ$, $[\alpha]_D^{18} -8.3^\circ$, soly. in AcOH at 20° 17.89%. *d*-Acid, obtained from the mother liquors of the *l*-acid through the *quinine salt* (needles, m. 135° (decompn.)), m. $157\text{--}8^\circ$, $[\alpha]_D^{20} 8.06^\circ$; *methyl ester*, m. 45° , $[\alpha]_D^{20} -11.1^\circ$. *dl*- δ -Truxinyl chloride, from the acid and PCl_5 or excess of SOCl_2 , m. 78° , is not very stable in the air, gives in Et_2O with cold concd. NH_4OH the *diamide*, fine felted micro-needles from Me_2CO , m. 224° ; *dianilide*, m. 283° , completely hydrolyzed to the acid by boiling 1 hr. with 30% alc. KOH but on very short heating it gives the *anilidic acid*, m. 225° . *l*- δ -Truxinic diamide, m. 206° , $[\alpha]_D^{18} 33.5^\circ$. C. A. R.

Investigations and ring closures in the series of the methylnaphthalenes. FRTZ MAYER AND ADOLF SIEGLITZ, with E. FISCHER, J. HAGEN, R. JUNG, W. KNIES, C. KOHL, F. LISTMANN, W. NEUGEBAUER AND TH. SCHULZE. *Ber.* 55B, 1835–59 (1922).—The original object of this investigation was solely to find the conditions under which a 5-membered ring can be added to C_{10}H_8 and to det. the constitution of the resulting tricyclic compd. but the surprising ease with which almost any desired aliphatic-aromatic C_{10}H_8 deriv. can be obtained by methods well known for the C_6H_6 series has lead to a study in this direction of the chemistry of C_{10}H_8 , which thus far has been investigated almost only in connection with dye stuffs. From 47.4 g. 1- $\text{C}_{10}\text{H}_7\text{Me}$ in CS_2 slowly treated with 53.2 g. Br, best in the dark, contrary to the statements of Schulze (*Ber.* 17, 1528 (1884)) and Scherler (*Ber.* 24, 3930 (1891)), and heated on the H_2O bath until the soln. is light yellow, are obtained 10% $\text{C}_{10}\text{H}_7\text{Me}$ b₁₂ up to 160° , 55% 1,4- $\text{C}_{10}\text{H}_6\text{MeBr}$ (A) b. $160\text{--}5^\circ$, 20% of 1- $\text{C}_{10}\text{H}_7\text{CH}_2\text{Br}$ (B) b. $165\text{--}95^\circ$ and 10% 1,4- $\text{C}_{10}\text{H}_6(\text{CH}_2\text{Br})_2$ (C), h. $195\text{--}210^\circ$. After repeated fractionation A b₁₂ $162\text{--}4^\circ$ and its picrate m. $123\text{--}4^\circ$. From A heated 2 hrs. with Mg and a drop of EtI in Et_2O and then treated 4 hrs. in ice with CO_2 is obtained 42% 1-methylnaphthalene-4-carboxylic acid, crystals from AcOH, m. 175° ; *methyl ester*, b₁₂ $192\text{--}4^\circ$; *ethyl ester*, b₁₂ 203° ; *chloride*, h₁₂ $150\text{--}60^\circ$; *amide*, needles from C_6H_6 , m. 193° ; *anilide*, needles from C_6H_6 , m. 179° ; *hydrazide*, from the Et ester refluxed

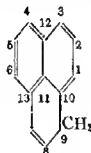
20 hrs. in alc. with $N_2H_4 \cdot H_2O$, silky needles from alc., m. 154° , gives, when treated in 2% HCl at 0° with 10% $NaNO_2$, then 10 min. with NO_2 , allowed to stand 10 min., shaken out with Et_2O , dried, dild. with alc., freed from the Et_2O and boiled 16 hrs., [4-methyl-naphthyl-1]-urethan, reddish needles from ligroin, m. 96° , which, refluxed 10 hrs. with 5 mols. alc. NaOH, gives 1,4- $C_{10}H_6MeNH_2$, m. 51° . 1-Methyl-4-benzoylnaphthalene, from $MeC_{10}H_7COCl$ and $AlCl_3$ in C_6H_6 on the H_2O bath, spears from C_6H_6 , m. $174-5^\circ$; heated 3 hrs. at 150° with 5 mols. $AlCl_3$ it gives 4-methyl-*peri*-benzanthrone (the notation I is used for *peri*-benzanthrones), olive rodlets from AcOH, m. 115° , sol. in H_2SO_4 with red-brown color. 4-Bromonaphthalene-1-carboxylic acid, from A hoiled with a mixt. of 110 g. HNO_3 (d. 1.4) and 1200 cc. H_2O , needles from AcOH, m. 212° ; methyl ester, needles from AcOH, m. 42° , b_{15} $195-200^\circ$; the acid in NaOH with $KMnO_4$ gives naphthalene-1,4-dicarboxylic acid, rodlets from AcOH, m. 288° ; dimethyl ester, spears from AcOH, m. 64° , b_{12} $195-7^\circ$. From 240 g. 1- $C_{10}H_7Me$ brominated according to Wislicenus in the light of an arc lamp (C. A. 11, 2783) are obtained 220 g. B, b_{14} $163-75^\circ$, and about 14 g. C, b_{11} $175-205^\circ$. B and Mg dropped into AcH in cold Et_2O give (1- $C_{10}H_7CH_2$) $_2$, m. $161-2^\circ$, which does not, as stated by Bamberger (Ber. 21, 54 (1888)), show any fluorescence in alc. Ethyl [1-naphthylmethyl]acetacetate (24 g. from 2 mols. $AcCH_2CO_2Et$ and 1 atom Na in C_6H_6 hoiled 15 hrs. with 1 mol. B), b_{12} $204.5-6.0^\circ$; 23.8 g. boiled 4 hrs. with 25 g. KOH in 90 cc. H_2O gives 10 g. 1-[1-naphthyl]-3-butanone, b_{11} $186-7^\circ$, reduced by Clemmensen's method to the butane, b_{11} $151-2^\circ$. Diethyl β -[1-naphthyl]isosuccinate (42 g. from 80 g. $CH_2(CO_2Et)_2$ and 5.8 g. Na in 100 cc. C_6H_6 heated 5 hrs. with 56 g. B), b_{11} 221° ; at the same time there are obtained 39 g. unchanged $CH_2(CO_2Et)_2$ and a nucleus-brominated 1-methylnaphthalene, b_{14} $161-2^\circ$ (picrate, m. $127-5^\circ$), apparently not identical with A; oxidation with CrO_3 -AcOH gives a small amt. of a $C_{10}H_6BrCO_2H$, spears from dil. AcOH, m. $215-8^\circ$. β -[1-Naphthyl]isosuccinic acid (17 g. from 22 g. of the ester sapond. 30 min. with 12 g. KOH in 25 cc. H_2O), crystals from H_2O , m. $160-3^\circ$, easily loses CO_2 at $170-80^\circ$, yielding 1- $C_{10}H_6CH_2CH_2CO_2H$, crystals from C_6H_6 , m. 151° , also obtained directly in 28 g. yield from 82 g. of the above ester by boiling with HCl in AcOH; heated 0.5 hr. at 80° with $SOCl_2$ the acid gives the chloride, b_{12} 187° ; amide, leaflets from C_6H_6 , m. 85° . The chloride (4.5 g.) in ligroin slowly added to 5 g. $AlCl_3$ in cold ligroin and finally heated 1.5 hrs. on the H_2O bath yields 1.4 g. 7,8-dihydro-g-phenalene (D), very unstable yellow leaflets, m. $85-6^\circ$; oxime, needles from alc., m. $124-5^\circ$ (the name phenalin, abbreviated from phenonaphthalene, is suggested for the mother substance of these *peri*-derivs., which are erroneously designated as *peri*-naphthindanones in Stelzner's Literatur-Register, p. 41, footnote 1, and p. 61, footnote 1, and the notation II is adopted). Diethyl β -[1-naphthyl]- α -ethylisosuccinate (104 g. from 140 g. $EtCH(CO_2Et)_2$, 200 cc. C_6H_6 , 11.6 g. Na and 112 g. B heated 8 hrs.), b_{12} 227° ; 115 g. heated 3 days with 46 g. KOH in 150 cc. alc. gives 75 g. of the acid, needles from C_6H_6 , m. $151-3^\circ$, 18 g. of which heated at $150-60^\circ$ gives 10 g. β -[1-naphthyl]- α -ethylpropionic acid, b_{15} $223-7^\circ$; ethyl ester, b_{14} $196-7^\circ$; chloride, b_{12} 183° ; amide, m. 132° . The chloride (20 g.) with 20 g. $AlCl_3$ in 80 cc. ligroin heated 2 hrs. on the H_2O bath gives 19.5 g. 8-ethyl-7,8-dihydro-g-phenalene (E), thick yellow oil, b_{14} 195° , gradually becomes dark red; 10 g. heated 5 days with 25 g. amalgamated Zn in 400 cc. H_2O and a total of 120 cc. concd. HCl gives 6 g. of 8-ethyl-7,8-dihydrophenalin, b_{14} $167-8^\circ$, while 13 g. with 10 g. $EtBr$ and 2.1 g. Mg in Et_2O gives 0.5 g. 7,8-diethylphenalin, yellow oil, b_{15} 185° , adds Br in the cold; 10 g. of this last compd. and 8 g. KOH in 300 cc. boiling H_2O treated in the course of 2 days with 94 g. $KMnO_4$ yields 0.95 g. hemimellitic acid, m. $188-9^\circ$. (This shows that in the formation of E, contrary to the observations of Sachs and Brigl (C. A. 5, 3427), the ring closure has occurred at the *peri*-positions.) 1- $C_{10}H_7CHO$, b_{15} $150-2^\circ$, is obtained in 21 g. yield from 44 g. B and 28 g. hexamethylenetetramine in 800 cc. of 60% alc. hoiled

6 hrs.; by working in CHCl_3 the hexamethylenetetramine addition product of **B** can be isolated, needles from alc., m. around $175-9^\circ$. α -[1-Naphthyl]- β -nitroethylene (7.5 g. from 10 g. 1- $\text{C}_{10}\text{H}_7\text{CHO}$ and 4 g. MeNO_2 in 20 cc. alc. and 5 g. of 50% aq. KOH in 8 cc. alc. at 5°), yellow needles from alc., m. 87.5° ; 4 g. treated 9 hrs. in cold Et_2O with 10 g. Al (as the amalgam) gives 1.9 g. 1-naphthylacetaldoxime, needles from CCl_4 , m. 118° ; this in alc. with 3% Na-Hg and AcOH gives β -[1-naphthyl]ethylamine, b_{18} $170-3^\circ$ (hydrochloride, m. $243-8^\circ$; acetyl derivative, needles from ligroin, m. 91°), also obtained by boiling 11.4 g. 1- $\text{C}_{10}\text{H}_7\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ 2 hrs. in 10 cc. abs. alc. with 12.5 g. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, which gives 10 g. of the hydrazide, needles from alc., m. $125-6^\circ$; 12 g. of this, diazotized in dil. HCl, taken up in Et_2O , dried, treated with abs. alc., freed from the Et_2O and boiled 2 hrs. longer after the evolution of N ceases yields 7 g. of the urethan, $\text{C}_{10}\text{H}_7\cdot\text{O}_2\text{N}$, pearly leaflets from ligroin, gives after refluxing 15 hrs. with alc. KOH 6 g. of the HCl salt of the above amine. 1-Bromomethyl-4-bromonaphthalene (**C**) seps. from ligroin in needles m. $103-4^\circ$, gives on boiling with alc. NaOEt [4-bromonaphthyl-1-methyl]ethyl ether, b_{17} $185-7^\circ$. 4-Bromonaphthyl-1-acetonitrile, from **C** and KCN in aq. alc., needles from ligroin, m. 82° , hydrolyzed by H_2O_2 in aq. alc. KOH to the acid, needles from ligroin, m. $140-50^\circ$; chloride, yellow oil, b_{12} $110-2^\circ$; amide, needles, m. 182° . The chloride with AlCl_3 in PhNO_2 at $80-90^\circ$ gives 5-bromo-1-acenaphthenone, needles from alc., m. $174-5^\circ$; oxime, needles from alc., m. $215-6^\circ$. Dichyl β -[4-bromonaphthyl-1]-isobutyrate, from $\text{CH}_3(\text{CO}_2\text{Et})_2$, Na and **C** in C_6H_6 , leaflets from AcOH, m. 55° , b_{14} 237° , converted by boiling HCl in AcOH into β -[4-bromonaphthyl-1]-propionic acid, leaflets from AcOH, m. 148° ; 15 g. of the chloride, b_{10} 195° (obtained in 2.5 g. yield from 5 g. of the acid), unexpectedly loses Br when heated with AlCl_3 in ligroin on the H_2O bath, giving 0.9 g. **D**. 4-Bromo-1-naphthaldehyde (4.5 g. from 20 g. **C** and 10 g. hexamethylenetetramine boiled 6 hrs. in 60% alc.), needles from MeOH, m. 85° . β -[4-bromonaphthyl-1]-acrylic acid, obtained quant. from 5 g. of the above aldehyde heated 16 hrs. at $160-5^\circ$ with 3.2 g. Ac_2O and 1.1 g. NaOAc, fine light yellow needles from AcOH, m. $250-1^\circ$. While Ruhemann was unable to effect a ring closure with 4,1- $\text{C}_{10}\text{H}_7\cdot(\text{OMe})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ (*C. A.* 14, 2643) it has been found that two 8-g. portions of the acid converted with SOCl_2 into the yellow viscous chloride and heated in ligroin with AlCl_3 yield 3 mg. **D**. 1,2- $\text{C}_{10}\text{H}_6\text{BrMe}$ (**F**), obtained like **A** (yield, 70%), b_{11} $165-70^\circ$, b_{125} $290-5^\circ$ (picrate, m. 113°), yields like **A** 60% of 2-methylnaphthalene-1-carboxylic acid, prisms from dil. AcOH, m. $126-7^\circ$, which cannot be esterified with alc. and HCl nor be oxidized to the di- CO_2H acid; chloride, b_{20} $170-2^\circ$; ethyl ester, through the chloride, b_{15} $180-3^\circ$; methyl ester, b_{16} $168-70^\circ$; amide, from C_6H_6 , m. 143° ; anilide, from MeOH, m. $167-8^\circ$. The esters yield no hydrazide when boiled with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. When the chloride is shaken with 0.5 part $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in Et_2O and the ppt. is washed with H_2O there remains undissolved bis-[2-methyl-1-naphthoyl]hydrazine, crystals from AcOH, m. 234° , while the aq. soln. contains the hydrazide, cubes from alc., m. 164° ; this in AcOH at 0° with NaNO_2 gives [2-methylnaphthyl-1]-urethan, crystals from AcOH, m. 135° , which is hydrolyzed to 1,2- $\text{C}_{10}\text{H}_6(\text{NH}_2)\text{Me}$. 2-Methyl-1-benzoylnaphthalene, from $\text{MeC}_6\text{H}_4\text{HCOCl}$ and AlCl_3 in C_6H_6 , prisms from alc., m. 74° , b_{14} $240-5^\circ$, also obtained from 2- $\text{C}_{10}\text{H}_7\text{Me}$ and BzCl with AlCl_3 in CS_2 ; 12 g. heated with 40 g. AlCl_3 2 hrs. each at 90° , 110° and 130° gives 6-methylbenzanthrone, bronze-colored leaflets from AcOH, m. 195° . 1,2- $\text{C}_{10}\text{H}_6\text{Me}_2$, from **F** and **Mg** in Et_2O with Me_2SO_4 , b_{11} 137° , $d_{4^{20}}^{20}$ 1.0118, $d_{4^{20}}^{20}$ 1.011, n_D^{20} 1.60691, 1.61461, 1.63613, for α , β and γ at 19.9° , n_D^{20} 1.6142. 2-[Bromomethyl]-naphthalene (**G**), obtained like **B** in 60-5% yield, b_{11} $168-72^\circ$, gives with **Mg** and AcH in Et_2O (2- $\text{C}_{10}\text{H}_7\text{CH}_2$) $_2$, crystals from CHCl_3 , m. 182° , identical with Friedmann's product (*C. A.* 11, 941), thus confirming his belief that Bamberger's compd. (*Ber.* 21, 54(1888)) is the unsym. $(\text{C}_{10}\text{H}_7)_2\text{CHMe}$. Ethyl [2-naphthylmethyl]acetate (67 g. from 12 g. Na, 200 cc. alc., 160 g. AcCH_2OEt and 11 g. **G**), b_{14} $218-20^\circ$; 67 g. heated

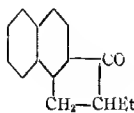
6 hrs. with 20 g. KOH in 60 cc. MeOH gives 6 g. $2\text{-C}_{10}\text{H}_7\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ and 25 g. $1\text{-[2-naphthyl]-3-butanone}$, crystals from alc., m. 50° , b_{11} 190–200°; *oxime*, needles from alc., m. $115\text{--}6^\circ$; *semicarbazone*, needles from alc., m. 173° . $1\text{-[2-Naphthyl]butane}$, b_{11} 125–30°. *Diethyl $\beta\text{-[2-naphthyl]isobutyrate}$* , b_{11} 214–6° (if C_6H_6 is used instead of alc. in its prepn. there is also obtained $2\text{-naphthylmethyl} \text{ethyl ether}$, b_{11} 148–51°); *free acid*, needles from C_6H_6 , m. $94\text{--}5^\circ$, yields by loss of CO_2 79% of $2\text{-C}_{10}\text{H}_7\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, leaflets from alc., m. $134\text{--}5^\circ$; *chloride*, obtained in 55% yield with 3 parts SOCl_2 , crystals from ligroin, m. 54° , gives on heating 2–3 hrs. in ligroin with AlCl_3 in very small yield $4,5\text{-benzo-1-indanone}$, needles from ligroin, m. 103° , sol. in H_2SO_4 with yellow color and blue fluorescence. *Diethyl $\beta\text{-[2-naphthyl]-}\alpha\text{-ethylisobutyrate}$* (120 g. from 112 g. G), b_{11} 225–7°; *free acid*, crystals from C_6H_6 , m. 150° . $\beta\text{-[2-Naphthyl]-}\alpha\text{-ethylpropionic acid}$ (yield, 72%), b_{11} 225–7°; *ethyl ester*, b_{11} 195–6°; *chloride*, b_{11} 190–5°; *amide*, needles from C_6H_6 , m. 108° . The chloride heated 2–3 hrs. in ligroin with AlCl_3 gives $2\text{-ethyl-4,5-benzo-1-indanone}$ (III), needles from MeOH, m. 54° , b_{11} 195–200°, reduced by Clemmensen's method to $2\text{-ethyl-4,5-benzointhane}$, b_{11} 157–60°, and converted by means of EtMgBr into $2,3\text{-diethyl-4,5-benzoindene}$, b_{11} 205–7°. Heated 24 hrs. at $160\text{--}70^\circ$ with a mixt. of 2 vols. $\text{HN}(\text{O})_2$ (d. 1.51) and 1 vol. H_2O , III yields mellophanic acid, m. 235° , showing that in III the new ring is formed, as expected, in the angular and not the linear position. $2\text{-C}_{10}\text{H}_7\text{CHO}$, m. 61° , b_{11} 155–60°, is obtained in 70–80% yield from G and hexamethylenetetramine heated 12 hrs. on the H_2O bath in 60% alc.; the *hexamethylenetetramine addition product* of G, colorless leaflets, decomp. 160° . $\alpha\text{-[2-Naphthyl]-}\beta\text{-nitroethylene}$ (yield, 70%), yellow needles from alc., m. 123° . $2\text{-Naphthylacetaldoxime}$, needles from CCl_4 , m. 120° . $\beta\text{-[2-Naphthyl]ethylamine}$, b_{11} 160–5°; *hydrochloride*, m. 250° (decomp.); *acetyl derivative*, crystals from ligroin, m. $109\text{--}10^\circ$. $1\text{-Bromo-2-bromomethylnaphthalene}$ (H), needles from alc., m. $107\text{--}8^\circ$. $1\text{-Bromonaphthyl-2-methyl cyanide}$, needles from alc., m. 127.5° , hydrolyzed to $1\text{-bromonaphthyl-2-acetic acid}$, needles from AcOH, m. 194° , whose *methyl ester* b_{11} 210–5°. $1\text{-Bromo-2-naphthaldehyde}$, from H and hexamethylenetetramine, needles from AcOH, m. 118° ; *oxime*, m. $164\text{--}6^\circ$. $1\text{-Bromonaphthalene-2-carboxylic acid}$, needles from AcOH, m. 136° . *Diethyl $\beta\text{-[1-bromonaphthyl-2]-isobutyrate}$* , leaflets from alc., m. $79\text{--}80^\circ$, b_{11} 250–60°. $\beta\text{-[1-Bromonaphthyl-2]-propionic acid}$, leaflets from alc., m. 125° ; *methyl ester*, crystals from AcOH, m. $86\text{--}7^\circ$; *chloride*, b_{11} 210–20°; *amide*, needles from C_6H_6 , m. 164° . $4\text{-Bromo-5,6-benzo-1-indanone}$, from the chloride heated 2 hrs. with AlCl_3 in CS_2 , crystals from AcOH, m. 152° (yield, poor); *oxime*, m. $222\text{--}5^\circ$ (decomp.); the ketone on reduction by Clemmensen's method and



I



II

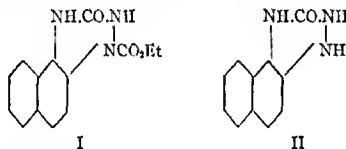


III

dehydrobromination gave a not quite pure *hyrindene*, m. 92° . (It is difficult to see how 4,5-benzo-1-indanones (III) are obtained by ring closure from $\beta\text{-[2-naphthyl]propionyl}$ chlorides.—ABSTR.) C. A. R.

Azo-ester reaction of amines and enols. OTTO DIELS. *Ann.* 429, 1–55(1922); cf. C. A. 15, 2086.—All aromatic amines react with azo esters with the formation of addn. products, the nature of which depends upon the kind of amine used. There appear to be 3 classes: $\text{C}_{10}\text{H}_7\text{NH}_2$ type, the addn. product of which contains the mol. of azo ester firmly bound to the nucleus; PhNH_2 type, the addn. product of which easily

decomps. into its components; the PhNMe_2 type, the addn. product of which is split by acid into HCHO , hydrazo ester and an amine contg. 1 less Me group. The importance of this reaction is especially seen in the fact that a large group of compds.—the amines—which appear to be structurally identical, may be transformed into derivs. corresponding to very different types. *1-Amino-4-dicarbethoxyhydrazinonaphthalene hydrochloride*, carbonizes above 200° , quickly hydrolyzed by cold H_2O into the base. The free base is sapond. by HI , giving $1,4\text{-C}_{10}\text{H}_6(\text{NH}_2)_2$. $\text{H}_2\text{NC}_6\text{H}_4\text{SO}_3\text{Na}$ and $(\text{NCO}_2\text{Et})_2$ (A) in 80% alc. give sodium *1-amino-2-dicarbethoxyhydrazinonaphthalene-4-sulfonate* (B), m. $204\text{--}10^\circ$ (decompn.). Boiled with $\text{C}_6\text{H}_{11}\text{N}$ for 4 hrs., B gives a new ring compound, $\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}_2\text{S}$ (C), yellow, decomp. above 135° , while with KOH and EtOH CO_2 and 2 EtOH are split off, giving the compound $\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}_2\text{S}$ (D), also obtained by heating C with alc. KOH for a long time, needles, m. about 330° . The reduction of B with 2.5% Na-Hg gives *1-amino-2-dicarbethoxyhydrazinonaphthalene* (E), needles, m. 147° . Distd. with HI and AcOH in a stream of CO_2 , it yields 2-methyl- β -naphthimidazole. E, boiled with $\text{C}_6\text{H}_{11}\text{N}$ for 5 hrs., gives the compound $\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}_2$ (F), needles, m. $272\text{--}3^\circ$ (this contains the same ring complex as C); heated with alc. KOH , E or I gives



II, needles, sinters 280° , m. 299° . The yields of D and II are very small. $(\beta\text{-C}_6\text{H}_4)_2\text{NH}$ and A, heated in alc. 15 hrs. at 100° , gave a very small yield of a compound, $\text{C}_{24}\text{H}_{20}\text{O}_4\text{N}_4$, small needles from $\text{C}_2\text{H}_5\text{Cl}$, m. $250\text{--}2^\circ$. *meso*-Anthraniline and A give *p*-amino-1,4-dicarbethoxyhydrazinonaphthalene (F), glistening light yellow prisms, m. 199° . The alc. soln. has a green fluorescence. Heated with Ac_2O for about 5 min., a monoacetate results, yellowish needles, m. 277° (decompn.). If the boiling is continued for an hr. the diacetate is formed, nearly colorless needles, m. $219\text{--}20^\circ$. One Ac group can be split off by heating with very dil. Na_2CO_3 . F adds EtO_2CNCOC , giving a compound, $\text{C}_{24}\text{H}_{20}\text{O}_8\text{N}_4$, prisms, m. 220° . The reaction of PhNH_2 and A gives phenyldicarbethoxytriazan (C. A. 6, 364), leaflets and prisms, m. 138° . *p*-Tolyl derivative, leaflets, m. 113° . This is decompd. by concd. HCl at 0° and also by boiling with Ac_2O , *p*- $\text{MeC}_6\text{H}_4\text{NH}_2\text{-HCl}$ being formed in the 1st case and *p*- $\text{MeC}_6\text{H}_4\text{NHAc}$ in the 2nd. Boiled with PhMe for 1.5 hrs., the soln. became dark red, and on cooling the hydrazo ester sepd. The residue was sepd. into 2 parts, b₁₂ $95\text{--}140^\circ$ and $140\text{--}60^\circ$. The 2nd fraction proved to be *p*-azotoluene. From the 1st, after distn. and sepn. into fractions by means of H_2SO_4 , *p*- $\text{MeC}_6\text{H}_4\text{NH}_2$ was found in the part sol. in H_2SO_4 , while ethyl *p*-methylcarbanilate, $\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}_2$, h. $243\text{--}7^\circ$, h₁₂ $128\text{--}32^\circ$, was isolated from the insol. part. *p*- $\text{MeC}_6\text{H}_4\text{NH}_2$ and A give 3-amino-6-dicarbethoxyhydrazino-1,4-dimethylbenzene (G), m. 117° ; from MeCN it crysts. with 1 mol. of MeCN , m. 84° . Hydrochloride, crystals from dil. HCl . Oxalate, m. 176° . Acetate, felted crystals, m. 193° . Sapond. with HI G yields 3,8,1,4- $(\text{H}_2\text{N})_2\text{C}_6\text{H}_3\text{Me}_2$ while concd. H_2SO_4 gives *p*-xyloquinone. The reaction of 3 g. *p*- $\text{MeC}_6\text{H}_4\text{NH}_2$, 8 g. A and 10 cc. dry Et_2O gives a compound, $\text{C}_{20}\text{H}_{19}\text{O}_4\text{N}_2$, contg. 2 mols. A, m. 168° . It is easily decompd. by acids and alkalis. Ac_2O splits off 1 mol. A, giving the acetate of G. 2-Dimethylamino-1-dicarbethoxyhydrazinonaphthalene, 6-sided tablets, m. 163.5° ; yield 70%. The perchlorate is the most characteristic salt, 6-sided tablets, m. 124° ; it is very hygroscopic and is explosive. The same compd. may be obtained by the action of MeI and NaOH upon the simple NH_2 deriv. (C. A. 15, 2086). 1-Dimethylamino-4-dicarbethoxyhydrazinonaphthalene, in 55% yield, 4-sided

monoclinic tablets, m. 154°. The salts are very sol. and difficult to obtain in a state of analytical purity. The corresponding *1*-monomethylamino derivative m. 193°. The unsubstituted base forms short prisms, m. 203-4°, and yields a mixt. of the above 2 bases on treatment with MeI. They may be sepd. by crystn. from AcOH or MeCN. *2*-Amino-1-dicarboxymethoxyhydrazinonaphthalene (H), by the action of $(\text{NCO}_2\text{Me})_2$ upon $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$, pale salmon crystals, m. 210°. Acetate, needles, m. 244°. Hydrochloride, m. 218°, is easily hydrolyzed by H_2O at room temp. The action of $\text{C}_6\text{H}_5\text{N}$ gives a compound $\text{C}_{10}\text{H}_6\text{ON}_3$, isomeric with II, pale brown prisms, m. 315°. H_2O_2 oxidized H to a compound, $\text{C}_{10}\text{H}_7\text{N}(\text{CO}_2\text{Me})\cdot\text{N}(\text{CO}_2\text{Me})\cdot\text{NOH}$, glistening prisms, m. 117°.

1-Amino-4-dicarboxymethylamidohydrazinonaphthalene, by the use of $(\text{NCONHMe})_2$, m. 214°. The corresponding ethyl derivative, small needles, m. 213°. Hydrochloride, begins to decomp. 160°, m. 285°. Heating with $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 gives $\text{C}_{10}\text{H}_6\text{O}_2$. *2*-Amino-1-dicarboxymethylamidohydrazinonaphthalene (J), m. 230°. Alc. KOH splits off MeNH_2 , giving a naphthimidazolone deriv., $\text{C}_{10}\text{H}_6\text{N}(\text{NHCONHMe})\cdot\text{CO}\cdot\text{NH}$,

m. 220-1°. HI transforms J into *1,2*-naphthyleneurea (*2*-keto-2,3-dihydro- α,β -naphthimidazole), also obtained by the action of COCl_2 upon $1,2\text{-C}_{10}\text{H}_6(\text{NH}_2)_2$, m. 377°. $(\text{NBz})_2$ gives an addition product, $\text{C}_{20}\text{H}_{12}\text{O}_2\text{N}_4$, with $\beta\text{-C}_{10}\text{H}_7\text{NMe}_2$, light salmon hexagonal rhomboids and prisms, m. 214-5°. The yield is about 15%. Hydrochloride, microcryst. powder. Potassium compound, rods, m. 200° (decompn.). The addition product of $\text{MeC}(\text{NH}_2)\cdot\text{CHCO}_2\text{Et}$ and $(\text{NCO}_2\text{Et})_2$ m. 88°, when shaken with dil. H_2SO_4 , splits off NH_3 and forms ethyl α -dicarbethoxyhydrazinoacetate (K), $\text{AcCH}[\text{N}(\text{CO}_2\text{Et})\text{NH}(\text{CO}_2\text{Et})]\text{CO}_2\text{Et}$, long tablets, m. 75°. The product when $(\text{NCO}_2\text{Me})_2$ is used is ethyl α -dicarbomethoxyhydrazine- β -aminocrotonate, m. 140°; this also loses NH_3 when shaken with dil. H_2SO_4 or when boiled with $\text{AcCH}_3\text{CO}_2\text{Et}$, giving ethyl α -dicarbomethoxyhydrazinoacetate, m. 113°. K is also formed when A is warmed with $\text{AcCH}_3\text{CO}_2\text{Et}$. The reaction of AcCH_3COMe and A gives β -dicarbethoxyhydrazinoacetylacetone, glistening needles, m. 123°. The corresponding methyl compound m. 120°.

C. J. WEST

Hydroxynaphthoquinone studies. V. Derivatives of 2-bromo-5-hydroxy-1,4-naphthoquinone (monobromojuglone). A. S. WHEELER AND B. NAIMAN. *J. Am. Chem. Soc.* **44**, 2331-4 (1922); cf. *C. A.* **16**, 1090.—A further study of monobromojuglone (A) has shown that it is very reactive. The method of prep. it has been so improved that the yield is more than doubled (6.1 g. from 5 g. juglone). No K salt could be obtained by treatment in Et_2O with aq. K_2CO_3 ; attempted oxidation with HNO_3 (d. 1.15) at 180° gave no product which could be identified. 2-Bromo-5-benzoy-1,4-naphthoquinone (0.44 g. from 0.5 g. A refluxed 3 hrs. in 5 cc. BzCl), lemon-yellow needles from C_6H_6 , m. 222°. 2-Chlorojuglone (0.45 g. from 0.7 g. A heated on the H_2O bath with 0.5 g. HCl in 50 cc. abs. alc. until completely dissolved), light brown flat needles from alc., m. 164°, gives with BzCl 2-chloro-5-benzoy-1,4-naphthoquinone, lemon-yellow needles from C_6H_6 , m. 222°. 2,3-Dibromo-5-hydroxy-1,4-naphthoquinone (2,3-dibromojuglone) (0.2 g. from 0.25 g. A and 0.1 cc. Br in 10 cc. AcOH heated 3 hrs. on the H_2O bath), fine gold-bronze needles from CCl_4 , m. 169°; 0.4 g. refluxed 6 hrs. in Ac_2O yields 0.5 g. of the 5-acetate, light yellow needles from alc. or AcOH , m. 172°. 2,3-Dichlorojuglone, from the di-Br compd. in alc. HCl on the H_2O bath, golden brown needles from alc., m. 153°. When the di-Br compd. is heated 1 hr. on the H_2O bath in 80 parts alc. and 40 parts of 10% NaOH , poured into 100 parts H_2O and acidified with dil. H_2SO_4 , a bromodihydroxynaphthoquinone seps. in yellow needles, m. 190°, sol. in alc. with deep red color and on addn. of a few drops of H_2O seps. in red needles with H_2O , turns brownish yellow about 80°, m. 192°.

C. A. R.

Anthracene series. III. E. DEBARRY BARNETT, J. W. COOK AND H. H. GRAINGER.

J. Chem. Soc. **121**, 2059-69(1923); cf. *C. A.* **16**, 3087.—Br in C_6H_5N does not react with 9,10- $C_{14}H_2Cl_2$, $C_{14}H_2Br_2$ or $C_{14}H_2(NO_2)_2$. *9-Nitroanthranthyl-10-pyridinium bromide*, $C_{14}H_9O_2N_3Br \cdot 2H_2O$, from 9- $C_{14}H_2NO_2$ and Br in C_6H_5N or by nitrating anthranthyl-9-pyridinium nitrate, pale yellow plates, m. $221-2^\circ$. The hydrogen sulfate forms a yellow powder, does not m. 300° . The aq. soln. gives a dark red ppt. with dil. NaOH. *Dichromate*, glistening orange leaflets with $2H_2O$, forming a yellow powder when dried. *Nitrate*, golden yellow plates with 0.5 H_2O . *Picrate*, yellow needles, m. $261-3^\circ$. In CCl_4 9- $C_{14}H_2NO_2$ reacts with Br to give the 9,10-Br $_2$ deriv., owing to the displacement of the NO_2 group. C_6H_5N converts chloronitrodihydroanthracene into 9- $C_{14}H_2NO_2$ and trinitrodihydroanthracene into $C_{14}H_2(NO_2)_3$. This is a very convenient method for prepn. of the latter compd. *9-Hydroxyanthranthyl-10-pyridinium bromide (anthronyl-pyridinium bromide)*, from bromoanthrone and C_6H_5N , by boiling for 15 min. or standing in $CHCl_3$ soln. at 0° for 2 hrs., pale yellow needles with 0.5 H_2O , m. $185-8^\circ$ (decompn.). *Nitrate*, much less sol. than the bromide. Bromodianthrone is obtained from bromoanthrone by the action of NH_3 , Et_3N , Pr_3N , Am_3N , iso-Bu $_3N$, α -picoline, and C_6H_5N . Dianthrone results when $MeNH_2$, Me_2NH , $C_6H_{11}N$, $PhNHMe$, $PhNMe_2$ or $PhNHCH_2Ph$ is used. Et_3NH gives dianthraquinone. 9,10- $C_{14}H_2Cl_2$ is conveniently prepd. by suspending 90 g. $C_{14}H_{10}$ in 650 cc. CCl_4 and adding 135 g. SO_2Cl_2 . After 24 hrs. at room temp. the soln. is cooled and the ppt. recrystd. from CCl_4 giving an almost theoretical yield.

C. J. WEST

1-Hydroxylaminoanthraquinone and some of its derivatives. W. H. BEISLER with L. W. JONES. *J. Am. Chem. Soc.* **44**, 2296-306(1922).—The deep color of the NHOH derivs. of anthraquinone and the remarkable change in color produced by dissolving them in alkalies are characteristic only of this particular class of β -hydroxylamine derivs. The present work was begun with the intention of studying the hydroxylaminoanthraquinone (A) obtained by reducing 1-nitroanthraquinone (B) in more detail than had previously been done; a study of this kind might be expected to bring to light other irregularities in the behavior of A which could be traced to some influence exerted by the anthraquinone nucleus. B. and J. believe, however, that the correct explanation for the colors of A and its salt will not be definitely established until the study is carried considerably beyond the scope of the present work. Pure anthraquinone, light yellow needles from $PhNH_2$, m. $277-8^\circ$, was obtained in 80-5% yield from anthracene and $Na_2Cr_2O_7$ in boiling H_2O slowly treated with $H_2SO_4 \cdot H_2O$; this with boiling fuming HNO_3 (d. 1.60) gives about 40% pure B, amber-colored tetragonal prisms from Me_2CO , m. $232.5-3.5^\circ$ (cor.), reduced by K_2S in boiling H_2O to the NH_2 compd., bright red needles with distinct greenish sheen from abs. alc., m. $252-3^\circ$ (cor.). From 8 g. B slowly added to 200 cc. C_6H_5N satd. at 0° with H_2S is obtained 6.5 g. A, maroon clusters from $MeOH$, decomp. without showing a definite m. p.; its SO_2H deriv. dyes wool and silk without a mordant in red-brown shades comparatively stable to light; treated in Me_2CO with the calcd. amt. of KOEt it yields the K salt, dark green when wet, red-brown when dry, difficultly sol. in H_2O , more readily in aq. Me_2CO , with characteristic deep blue-green color; after exposure to the air for 4 days the solid salt no longer gives the blue-green color with these solvents. Treated in dil. NaOH with air, A is converted in 3-4 hrs. into 1-nitrosoanthraquinone, old-rose needles from alc., m. $223-4^\circ$, gives the Liebermann reaction with $PhOH \cdot H_2SO_4$ is reduced back to A by K_2S or $H_2S \cdot C_6H_5N$; H_2O_2 can be detected in the filtrate from the NO compd. Refluxed in $PhMe$ with $PhNCO$, A yields the urea $C_6H_4(CO)_2C_6H_5N(OH)CONHPh$, dark red-brown needles, m. 236° , hydrolyzed by concd. HCl at 200° to CO_2 and $PhNH_2$. A almost instantly reduces cold $NH_4 \cdot AgNO_3$ but has very little action on Fehling soln.; it does not combine with AcH even in a sealed tube at 100° , can be recrystd. without change from boiling BzH , dissolves in strong acids, yields no NO deriv. with HNO_3

in the presence of a mineral acid, reacts with AcCl and BzCl in alk. soln., presumably with formation of an acyl deriv., gives with PbN:NPh in alk. soln. a brown powder, m. about 140° (decompn.). C. A. R.

Pyrroles. I. Pyrrolealdehydes. HANS FISCHER AND WERNER ZERWECK. *Ber.* 55B, 1942-9(1922).—Pyrrolealdehydes can be obtained in good yields by use of the Gattermann synthesis with anhyd. HCN and HCl in abs. Et_2O . Thus, when 5 g. 2,4-dimethyl-3-carbethoxypyrrole (A) in 50 cc. Et_2O and 3 cc. HCN is satd. in the cold with HCl and the resulting brownish needles of the imine- HCl are filtered off after standing several hrs. at room temp., washed with dry Et_2O , taken up in cold H_2O , filtered and beaten on the H_2O bath there is obtained 5.55 g. 2,4-dimethyl-3-carbethoxy-5-formylpyrrole (B), needles from alc. or H_2O , m. 165° , sol. in cold concd. HCl , reprecip. by NaOH , gives in the cold a negative, on heating a positive aldehyde reaction with $p\text{-Me}_2\text{NC}_6\text{H}_4\text{-CHO}$, produces no red color with fuchsin- SO_2 , is not volatile with steam; phenylhydrazone, faintly yellowish needles from $\text{EtOH-H}_2\text{O}$, m. 163° ; oxime, m. 168.5° , sol. in NaOH and HCl ; semicarbazone, m. 229° . Concd. HNO_3 converts B into 2,4-dimethoxy-3-carbethoxy-5-nitropyrrole, m. 148° . Boiled 1 min. with dil. HCl B gives bis-[2,4-dimethyl-3-carbethoxypyrrolyl]methane- HCl (C), m. 213° , the B condensing with itself with elimination of HCO_2H , the mol. which loses the CHO group probably rearranging into the pyrrolenine form, $\text{EtO}_2\text{CC:CMc.CH}_2\text{N:CMe}$, which then condenses with

another mol. of B; this view is confirmed by the fact that C is also obtained in 0.35 g. yield from 0.2 g. B and 0.18 g. A heated a few min. on the H_2O bath with 2 cc. concd. HCl . Unexpectedly, B and 2,5-dimethyl-3-carbethoxypyrrole with concd. HCl also give C. Heated 1 hr. on the H_2O bath with hippuric acid, NaOAc and Ac_2O , B yields the condensation product $\text{C}_{15}\text{H}_{19}\text{O}_4\text{N}_2$, orange-yellow needles from AcOEt , m. 175° . 2,5-Dimethyl-3-carbethoxy-4-formylpyrrole (yield, 76.5%), needles from H_2O , m. $151\text{--}1.5^\circ$; phenylhydrazone, faintly yellowish needles from dil. alc., m. 145.5° ; with A the aldehyde gives C and with hippuric acid a condensation product, yellow needles with red-brown surface luster from AcOH , m. 195° . 2,4-Dimethyl-5-formylpyrrole, stout needles from H_2O , m. 90° . II. Nitration of substituted pyrroles. *Ibid* 1949-55.—The nitration of alkylated pyrroles proceeds with the greatest smoothness. If a $\beta\text{-Ac}$ or $\beta\text{-CHO}$ group is present it is replaced by NO_2 , but a $\beta\text{-CO}_2\text{H}$ group has no such directing influence; 2,4-dimethyl-3,5-dicarbethoxypyrrole (A) does not lose its CO_2Et groups but the two Me groups are replaced by NO_2 groups. 2,4-Dimethyl-3-carbethoxy-5-nitropyrrole, from the 5-Ac deriv. allowed to stand several hrs. with HNO_3 (d. 1.4), needles from dil. alc., m. 149.5° , sol. in dil. NaOH with yellow color, reacts neutral to litmus in Et_2O , gives no Ehrlich reaction with $p\text{-Me}_2\text{NC}_6\text{H}_4\text{CHO}$ even on heating, is also obtained by the action of concd. HNO_3 on the 5-CHO deriv. and on bis-[2,4-dimethyl-3-carbethoxypyrrolyl]methane and -methene; treated in very dil. NaOH with 22% NaOH until a thick ppt. results and then allowed to stand several hrs. at room temp., it hydrolyzes to 2,4-dimethyl-5-nitropyrrole-3-carboxylic acid, needles, m. 231° (gas evolution), also obtained from the 5-Ac acid gradually added to concd. HNO_3 . 2,4-Dimethyl-3-nitro-5-carbethoxypyrrole, similarly obtained from the 3-Ac deriv., needles from dil. alc., m. 204° , easily sol. in dil. NaOH , hydrolyzed by refluxing 45 min. with 2% NaOH to the 5-carboxylic acid, darkens 240° , carbonizes on bigger heating. 2,4-Dinitro-3,5-dicarbethoxypyrrole, from A and concd. HNO_3 , faintly yellowish tables with 1 H_2O from alc., m. 136° (gas evolution), sol. in dil. NaOH and Na_2CO_3 with yellow color, reacts acid to litmus in Et_2O ; heated above its m. p. or *in vacuo* at 100° it quant. loses its H_2O of crystn. and 2 mols. NO , yielding what is in all probability a diketopyrrole. C. A. R.

Reactions of the formamidines. X. The thioimidazolones. F. B. DAINS, RUTH THOMPSON AND W. F. ASENDORF. *J. Am. Chem. Soc.* 44, 2310-5(1922); cf. C. A. 15, 3104.—The H of the $\text{CH}_2 =$ grouping in thioimidazolones reacts with the substituted

formamidines just as readily as that of the CH_2 grouping of pyrazolones, isoxazolones, thiazolidones, etc.; $\text{XYCH}_2 + \text{RNHCH:NR} = \text{XYC:CHNHR} + \text{RNH}_2$. 1,3-Di-phenyl-2-thio-5-anilinomethylene-4-imidazolone, from equimol. proportions of the imidazolone and PhNHCH:NPh heated 20 min. at $135-40^\circ$, m. 175° , is insol. in KOH. 1-Phenyl-3-*p*-tolyl homolog, yellow needles from alc., m. $197-8^\circ$. The following 3-aryl-2-thio-5-anilinomethylene-4-imidazolones, which are sol. in KOH and reprecipitated unchanged by acids, were similarly prepared: Phenyl, yellow needles, m. 252° ; *p*-tolyl, yellow plates, m. 250° ; *o*-tolyl, yellow crystals, m. 215° ; *m*-tolyl, yellow needles, m. $207-8^\circ$; *p*-chlorophenyl, light brown, m. $274-6^\circ$; *p*-ethoxyphenyl, pale yellow, m. 227° . 3-Phenyl-2-thio-5-*p*-bromoanilinomethylene-4-imidazolone, reddish brown needles, m. 190° ; 5- α -naphthylino analog, m. 160° . 3-*m*-Tolyl-2-thio-4-imidazolone, obtained in 90% yield from $\text{m-MeC}_6\text{H}_4\text{NCS}$, $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ and NaOH in $\text{H}_2\text{O-EtOH}$ at 100° , fine yellow needles from alc., m. 167° . 3-*p*-Chlorophenyl analog, yellow needles from alc., m. 234.5° . The following 3-phenyl-2-alkylmercapto-5-anilino-4-imidazolones were prepared from the imidazolone and 1 mol. NaOEt in alc. heated with the alkyl iodide until neutral: Methyl, m. 173° ; ethyl, m. 164.5° ; butyl, yellow needles, m. 124° ; allyl, greenish yellow, m. 218° . The 3-aryl-2-benzylmercapto-5-anilino-4-imidazolones were made by shaking the imidazolone in 40% KOH with PhCH_2Cl : Phenyl, yellow needles, m. 145° ; *o*-tolyl, m. 148° ; *m*-tolyl, m. 154° ; *p*-ethoxyphenyl, m. 170° , yellow needles. 1-Benzoyl-2-thio-3-phenyl-4-imidazolone (A), from PhNCS and hippuric acid at 150° , needles from alc., m. $177-9^\circ$; 3-*m*-tolyl homolog, m. 197° ; 3-*p*-ethoxyphenyl analog, greenish, m. 168° . 1-Benzoyl-2-thio-3-phenyl-5-anilinomethylene-4-imidazolone (B), needles, m. $184-6^\circ$; 3-*m*-tolyl homolog, m. 187° . 1-Benzoyl-2-thio-5-anilinomethylene-4-imidazolone, red needles from alc., m. $164-5^\circ$; 2-benzylmercapto compound, fine yellow needles, m. 185° . 2-Thio-5-anilinomethylene-4-imidazolone, deep red, m. 264° , sol. in NaOH. Refluxed 6 hrs. in a mixt. of 75 cc. alc. and 10 cc. concd. HCl, A yields PhNH_2 , a little BzOH and hippuric acid, the ring having evidently been opened and the resulting mustard oil hydrolyzed to PhNH_2 ; B behaved in the same way. Another case of ring opening was observed in efforts to prep. a PhCH_2 thioether of the unsubstituted thioimidazolone by treating in 20% NaOH with PhCH_2Cl ; instead of the expected ether being formed, the thiohydantoin was desulfurized with formation of $(\text{PhCH}_2)_2\text{S}_2$ and $\text{PhNHCONHCH}_2\text{CO}_2\text{H}$, m. 197° .

C. A. R.

Selenium organic compounds. I. Synthesis of 2-methyl-4-selenoquinazolone, 2-phenylbenzoselenazole, and some derivatives of the latter. M. T. BOGERT AND YÜ-GWAN CHEN. *J. Am. Chem. Soc.* 44, 2352-7 (1922).—*o*-Amino-benzoselenamide, rather unstable crystals from H_2O , m. 116° , is obtained in poor yield from $\text{o-H}_2\text{NC}_6\text{H}_4\text{CN}$ in abs. alc. satd. at 0° with dry H_2Se and NH_3 and heated 10 hrs. in a sealed tube at $105-10^\circ$. 2-Methyl-4-selenoquinazolone, $\text{NH}_2\text{C}_6\text{H}_4\text{N:CMe}$, obtained in 20-5%

yield from 20 g. $\text{H}_2\text{NC}_6\text{H}_4\text{CN}$ and 40 g. freshly prepd. Na_2Se at 115° in a N atm. slowly treated with 40 g. Ac_2O and kept 0.5 hr. longer at 110° , seps. from dil. alc. in brownish needles or prisms, m. 213.5° , readily sol. in alkalies, reprecipitated by CO_2 , slowly decomps. in the light and air with sepn. of finely divided Se and formation of 2-methyl-4-quinazolone. 2-Phenylbenzoselenazole (A), $\text{SeC}_6\text{H}_4\text{N:CPh}$, long needles from alc., m. 117.5° , is ob-

tained in 60% yield from 106 g. BzH and 93 g. PhNH_2 heated 2 hrs. at 120° , poured upon 100 g. Se dust and gently boiled 3 days under an air condenser; 25 g. in 150 cc. concd. H_2SO_4 slowly treated at 0° with 9.5 cc. concd. HNO_3 and 15 cc. concd. H_2SO_4 in the course of 30 min. and stirred 4 hrs. longer below 0° gives 95% of the 6-nitro derivative, flattened pale yellow needles from alc., m. 202.4° , converted by Sn and HCl, in 75% yield, into the amino compound, fine yellowish needles from alc., m. $201.2-2.3^\circ$, yields BzOH on fusion with KOH, showing that the NH_2 group is not in the 2-Ph nucleus; its acetyl derivative m.

188.1–8.7°, and the *benzal derivative*, obtained in 90% yield from the amine and BzH in alc., yellow plates from CS₂, m. 156.7–7.6°. *2-Phenylbenzoselenazole-β-naphthol*, from the diazotized amine and β-naphthol, deep red powder with metallic luster from EtOH-PhNH₂, m. 284.2°, dyes silk a fine pink. The diazotized amine was coupled with a no. of other phenols and amines, yielding red to brown dyes which dyes silk from red to brownish colors. *Dinitro-2-phenylbenzoselenazole*, obtained in 80% yield from 25 g. A in 150 cc. concd. H₂SO₄ slowly treated at 0° with 19 cc. HNO₃ and 30 cc. H₂SO₄ in 2 portions at a 2-hr. interval and then heated 2 hrs. at 100°, fine pale yellow needles from AcOH, m. 246.8°; the NO₂ groups are probably in positions 4 and 6; Sn and HCl give the *diamino compound*, needles from C₂H₅N, m. 269–70.5°, whose *diacetyl derivative*, cubes from dil. alc., m. 239.5–40.5, and *dibenzal derivative*, yellow plates from CS₂, m. 186–7°. The diazotized diamine coupled with various phenols and amines yielded the corresponding Se azo dyes.

C. A. R.

Quercitol and its derivatives. JOHN MISSENDEN. *Chem. News* 125, 120–1 (1922).—A brief review.

G. W. STRATTON

Reduction of flavanone. KARL FREUDENBERG AND LUDWIG ORTHNER. *Ber.* 55B, 1748–51 (1922).—*o*-HOCC₆H₄COMe, b_B 91–2°, is obtained in 37 g. yield from 100 g. AcOPh slowly treated with 200 g. AlCl₃ heated 5 hrs. at 120°, decompd. with ice and distd. with steam at 150°; 30 g. with BzH gives 39 g. *o*-HOCC₆H₄COCH:CHPh, 100 g. of which, refluxed in 20 g. portions 24 hrs. in 1 l. of 96% alc. with 100 cc. HCl (d. 1.19) and 240 cc. H₂O, the process being repeated with the unchanged chalcone which seps., yields 78 g. flavanone; 2 g. of this in 100 cc. of 80% alc. turbid 2–3 hrs. at 10–5° with 6 g. amalgamated Al gives 0.25 g. *flavanol* (*4-hydroxyflavan*), leaflets from 30% alc., m. 119°, gives no color with alc. NaOH, dissolves in concd. H₂SO₄ with deep violet-red color; *acetate*, from the flavanol heated 15 min. at 100° with 3 parts each of Ac₂O and C₂H₅N, short stout prisms from AcOH, m. 85–6°. A by-product in the prepn. of the

flavanol is a *pinacol* $\begin{array}{c} \text{O} \text{---} \text{CHPh} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \cdot \text{CH}_2 \\ | \\ \text{C}(\text{OH}) \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \text{---} \text{CHPh} \end{array}$, stout prisms from AcOH, m. about 250°,

colored wine-red by concd. H₂SO₄, unchanged by alc. NaOH, mol. wt. in boiling (CH₂)₂ 374–417.

C. A. R.

Cyanine dyes. VI. Dyes containing a quinoline and a benzothiazole nucleus. **The thioisocyanines.** W. T. K. BRAUNHOLTZ AND WM. H. MILLS. *J. Chem. Soc.* 121, 2004–8 (1922); cf. *C. A.* 16, 3184.—In general appearance the absorption spectra of the thioisocyanines are very similar to those of the isocyanines, but the bands in the former lie nearer to the blue end of the spectrum, the difference in wave length being roughly λ 500. The thioisocyanines are powerful photosensitizers for the green, giving an extra sensitization to the gelatino-bromide plate extending to about λ 5800. *2,1'-Diethylthioisocyanine iodide*, C₂₄H₂₂N₂IS, from C₂H₅N₂EtI and 1-methylbenzothiazole-EtI by the action of EtONa, bright red needles, m. 283°. The sensitization spectrum shows a powerful band in the green extending as far as about λ 5800 with a max. at λ 5250. The absorption max. lie at λ 5030 and about λ 4890, resp. *5-Methyl-2,1'-diethylthioisocyanine iodide*, bright red needles, m. 269–70° (decompn.). The absorption bands have max. at λ 5080 and about λ 4920. *1',6'-Dimethyl-2-ethylthioisocyanine iodide*, dark red prismatic needles, m. 306–7°. The 2 absorption max. lie at λ 5000 and about λ 4870. *5,1',6'-Trimethyl-2-ethylthioisocyanine iodide*, dark red needles, m. 303° (decompn.); the crests of the 2 absorption bands occur at λ 5070 and about λ 4950. *6'-Ethoxy-2,1'-diethylthioisocyanine iodide*, bright red needles when quickly crystd. from MeOH or short triclinic prisms terminated by domal planes by slow crystn., apparently

contg. 1 MeOH, m. 262° (decompn.). The absorption max. are at λ 5060 and λ 4930. 6'-Ethoxy-5-methyl-2,1'-diethylthioisocyanine iodide, bright red needles, m. 269° (decompn.), with absorption max. at λ 5110 and λ 4990. C. J. WEST

Quaternary salts of quinaldinic acid. WM. H. MILLS AND F. M. HAMER. *J. Chem. Soc.* 121, 2003-14(1922).—These salts are of interest because they are possible oxidation products of the isocyanines. *Methyl quinaldinate methiodide*, from the ester, which is conveniently prepd. by direct esterification of the acid in 80% yield, and Me_2SO_4 pale orange crystals, m. $122-9^{\circ}$ (decompn.). An aq. soln., shaken with Ag_2O , gave the *betaine*, large prisms, m. $142-5^{\circ}$ (decompn.). The *methochloride* results by the action of HCl upon the *betaine*, nearly colorless, m. $158-65^{\circ}$ (decompn.). *Methonitrate*, m. 138° (decompn.). *Cinnamylidenequinaldine ethiodide*, best prepd. by treating the sulfate with KI , red, m. $226-8^{\circ}$ (decompn.). *Ethobromide* (A), red, m. $213-1^{\circ}$. *Quinaldinic acid ethochloride*, by treating the nitrate (B) (*C. A.* 15, 829) with excess of concd. HCl satd. with SO_2 , m. 150° (decompn.). The *betaine* m. $146-8^{\circ}$ (decompn.) and is rather unstable. B was obtained by oxidation of A with HNO_3 . In the prepn. of B from pinacyanol it is possible to prove the presence of quinaldinaldehyde ethonitrate through the formation of a phenylhydrazone. C. J. WEST

Strophanthin. I. Strophanthidin. W. A. JACOBS AND MICHAEL HEIDELBERGER. *J. Biol. Chem.* 54, 253-61(1922); cf. Hefter and Sachs, *C. A.* 6, 1812; Windaus and Hermanns, *C. A.* 9, 2378, 2380; Brauns and Clossou, *C. A.* 7, 2994.—The seeds of *Strophanthus kombé* were ground, extd. with gasoline and then with 70% EtOH. The EtOH ext. was concd., *in vacuo*, to a thick sirup which was then dissolved in 2 parts, by wt., of H_2O and treated with an excess of $\text{Pb}(\text{OH})\text{OAc}$. The excess of Pb in the filtrate and washings was removed with H_2SO_4 , the filtrate from the PbSO_4 was acidified to Congo red with HCl and the mixt. was heated to $70-80^{\circ}$ for 3-4 hrs. About 25 g. crude strophanthidin crystd. from the ext. of each kg. of seeds. It was recrystd. from 95% EtOH. In 2.796% soln. in MeOH, $[\alpha]_D^{25}$ 43.1°. Compn. $\text{C}_{20}\text{H}_{20}\text{O}_6$. *Strophanthidin benzoate*, $\text{C}_{20}\text{H}_{20}\text{O}_7$, in 1.067% soln. in AcMe, $[\alpha]_D^{25}$ 47.8°. *p*-Bromobenzoate, $\text{C}_{20}\text{H}_{18}\text{O}_7\text{Br}$, decomp. $222-4^{\circ}$, in 1.094% soln. in AcMe $[\alpha]_D^{25}$ 42.0. *Oxime*, $\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}$, m. $270-5^{\circ}$, in 1.009% soln. in $\text{C}_6\text{H}_5\text{N}$ $[\alpha]_D^{25}$ 71.3°. *Phenylhydrazone*, $\text{C}_{20}\text{H}_{18}\text{O}_6\text{N}_2$, sinters 175° , m. $230-2^{\circ}$, in 1.00% soln. in CHCl_3 $[\alpha]_D^{25}$ -5.0° . *p*-Bromophenylhydrazone, $\text{C}_{20}\text{H}_{17}\text{O}_6\text{N}_2\text{Br}$, softens $180-53$, m. 200° , in 1.004% soln. in CHCl_3 $[\alpha]_D^{25}$ 105.5° . *Dihydrostrophanthidin*, $\text{C}_{20}\text{H}_{22}\text{O}_6$, by reduction with Pd and H_2 in MeOH, at room temp. for 2 weeks, m. and effervesces $100-3^{\circ}$, resolidifies and again m. $145-7^{\circ}$ or only sinters and then m. $190-5^{\circ}$, in 1.004% soln. in MeOH $[\alpha]_D^{25}$ 31.85° . *Benzoate*, $\text{C}_{20}\text{H}_{20}\text{O}_7$, m. $225-7^{\circ}$. *Isostrophanthidin*, $\text{C}_{20}\text{H}_{20}\text{O}_6$; *benzoate*, $\text{C}_{20}\text{H}_{20}\text{O}_7$, m. 270° , in 1.002% soln. in CHCl_3 $[\alpha]_D^{25}$ 38.0. All analyses were made on material dried at room temp. or 100° over H_2SO_4 or P_2O_5 . I. GREENWALD

Solubility and volatility of 3,5-dinitrophenol (SIDGWICK, TAYLOR) 2.

Oxalic acid. BADISCHE ANILIN & SODA-FABRIK. Brit. 184,627, June 7, 1921. Wood or other material contg. cellulose is treated with HNO_3 or with oxides of N and H_2O in the presence of a catalyst which may consist of a compd. of Fe, of rare earths or their compds., or of Mg compds. In examples, HNO_3 solns. of $\text{Fe}_2(\text{NO}_3)_6$ or of Di nitrate are used at temps. of about 60° ; with Mg compds. higher temps. are used, so that the salt is melted in the presence of H_2O ; the HNO_3 may be supplied from $\text{Mg}(\text{NO}_3)_2$ when employed as catalyst, by heating it to about $160-70^{\circ}$ and gradually adding the wood to the fused salt. When MgCl_2 is used, HNO_3 is added and the temp. raised to about $170-90^{\circ}$.

Acetylene. ELEKTIZITÄTWERK LONZA. Brit. 184,778, June 13, 1922. To the

alkali hypochlorite soln. used for removing phosphoretted and sulfuretted H from C_2H_2 , is added a substance such as alkali bicarbonate that prevents the soln. from contg. any considerable concn. of free HClO acid. When exhausted, the purifying soln. is regenerated electrolytically, preferably with the use of graphite anodes and an addn. of K_2CrO_4 .

Esters. P. HADDAN. Brit. 183,897, April 4, 1921. Org. acids, other than poly-HO fatty acids, are converted into esters by the aid of Zn, Sn, or other metal of the periodic group of which Sn is a member. Particular reference is made to the esterification of fatty and resin acids. Fats contg. free fatty acids can be neutralized by heating at ordinary or reduced pressure in the presence of Sn with the necessary quantity of glycerol or of the mono- or diglycerides of such acids as caprylic, lauric, myristic, stearic, oleic or erucic acid. Cf. 112,624.

Benzanthrone derivatives. BRITISH DYESTUFFS CORPORATION, LTD.; A. G. PERKIN and G. D. SPENCER. Brit. 183,351, July 12, 1921. Hydroxybenzanthrone is obtained by heating benzanthrone under pressure with caustic alkali soln. in the presence of anthraquinone, with or without additions of a chlorate or nitrate. Aminobenzantrone is obtained by heating the hydroxy compd. with strong NH_3 under pressure.

Thiohydriens. FARBWERKE VORM MEISTER, LUCIUS & BRÜNING. Brit. 185,408, Aug. 9, 1922. Propylenethiohydrin or propylene ethylene thiohydrin or mixts. thereof with ethylene thiohydrin, are obtained by action of alkali sulfides on propylene chlorohydrin (obtained from propylene and hypochlorous acid) or a mixt. thereof with ethylene chlorohydrin.

Aromatic amines. W. L. GALBRAITH, W. V. SHANNAN and N. E. SIDERFIN. Brit. 184,284, May 13, 1921. Aromatic amines are obtained by heating unsubstituted phenols with a mixt. of NH_3 and NH_4 salt other than sulfite (e. g., NH_4Cl), and an alkali sulfite. The alkali sulfite may be that contained in the crude melt resulting in the prepn. of the phenol from the corresponding sulfonic acid by alkali fusion. An example is given of the prepn. of β -naphthylamine. Cf. 1357, 1900.

11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

Comparative buffering value of American peptones. J. BRONFENBRENNER, G. C. DE BORD, and P. F. ORR. *Proc. Soc. Exptl. Biol. Med.* 19, 16(1921).—The p_H of the various peptone solns. was detd. electrometrically before and after the addition of measured amts. of acid and alkali, resp. The initial reactions of the different solns. varied greatly; so did their buffer actions at a given p_H , some being 5 times greater than others. The buffering effect varied at different zones of p_H , being most marked between p_H 9 and 8, and least between p_H 5 and 4. For a given peptone the buffering varied at different p_H zones; the absolute concn. of buffer salts was highest at the lowest p_H and not at neutrality or high p_H as would be most desirable in media for use in the identification of bacteria by cultural methods. The following peptones were studied: Difco, Proteose, Witte, Aminoid, Fairchild, Roche, and Armour. C. V. B.

The distensive agencies in the growth of the cell. D. T. MACDOUGAL. *Proc. Soc. Exptl. Biol. Med.* 19, 103–10 (1921).—Expts. were conducted with an artificial cell, the outer wall of which consisted of a fixed colloid of clay, wood, or parchment, and a lining or plasmatic layer of reversible gel consisting of agar, gelatin and various mixts. of these with K oleate, Ca oleate, lecithin and other substances. The jelly layer was

about 3 mm. thick, and the cell content 30 to 40 cc. The capsule was fitted with an osmometer head for measurement of vol. or pressure. It was so arranged that the cell could be subjected to a range of solns. externally and internally comparable to those of the living cell. Such cells filled with water and immersed in water show an intake and excretion for a continuous period of 60 to 80 days at 15°, during which time the vacuolar content of the cell is replaced 2 or 3 times; this demonstrates that all substances which may appear in the cell in the colloidal condition of reversible gels must be taken into account in any adequate interpretation of cell action. The artificial cell may be arranged to show exosmosis in its earlier stage, followed by endosmosis, and negative osmosis by the action of Ca or Mg salts as vacuolar contents or as immersion media. (The term "negative osmosis" is used to denote increase in vol. of the solvent in the cell against a soln. of higher concn. external to the cell.) As in living cell masses, the tonicity of the water-filled artificial cell can be raised by immersion in a series of increasing concns. The cell may prove of value in explaining the massing of material in plants, where diffusion or excretion seem to work against osmosis as in glandular action in animals.

C. V. B.

The diffusion of sodium chloride through a "lecithin"-collodion membrane. H. A. ABRAMSON AND S. H. GRAY. *Proc. Soc. Exptl. Biol. Med.* 19, 114(1921).—Solns. of collodion (4 g. guncotton per 100 cc.) and of "lecithin"-collodion (4 g. each of guncotton and com. "lecithin from eggs" per 100 cc.) were used to prep. a series of uniform membranes, varying in their drying time from 1.5 to 4 mins., this time being terminated by fixation with tap water. Permeability was detd. by filling with 0.25 M NaCl and immersing in beakers of water for 20 mins. Pure collodion membranes were all clear and had a const. diffusion rate. Lecithin-collodion membranes varied from clear to opalescent with the drying time, and the diffusion rate also increased with the drying time. Changes in the sizes of the aggregates of the lecithin mols. are suggested as a possible influence in varying the permeability of these membranes.

C. V. B.

Rigor mortis. ERNST MANGOLD. *Naturwissenschaften* 10, 895-9(1922).—A description of the chem. and phys. phenomena accompanying rigor mortis, with an extended bibliography.

C. C. DAVIS

A new zymophosphate. KARL SCHWEIZER. *Schweiz. Chem. Ztg.* 1920, 361.—The acceleration of alc. fermentation by phosphates was shown by Harden and Young to be due to the reaction: $2 C_6H_{12}O_6 + 2 Na_2HPO_4 \longrightarrow 2 CO_2 + 2 EtOH + C_6H_{10}O_4(Na_2PO_4)_2 + 2 H_2O$. Since, however, yeast contains an enzyme (phosphatase) which forms zymophosphates, the enzyme must be removed to make a quant. detn. of this phosphoric ester. This can be effected by drying yeast at a low temp. or by addn. of antiseptics. From the sodium compound $C_6H_{10}O_4(Na_2PO_4)_2$ and the potassium compound first obtained, the lead, silver, barium and calcium salts and the free acid $C_6H_{10}O_4(H_2PO_4)_2$ are obtained by treating the Pb salt with H_2S . The iron compound $C_6H_{10}O_4(Fe_2PO_4)_2$, formed by pptn. of an alc. soln. of the Na salt by $FeCl_3$, was an amorphous gray-green, odorless, tasteless powder, decomp. at 200°, hydrolyzed by acids and pptg. $Fe(OH)_3$ with NaOH. It can be used for anemia, chlorosis, etc., and on account of being insol. in H_2O is not injurious to the teeth. It is slowly decompd. in the stomach by acids and, like formerly used Fe and PO_4 compds., is not irritable to the gastrointestinal tract.

C. C. DAVIS

The question of complementary factors (vitamins). WALTER ROBINS. *J. pharm. Belg.* 4, 677-81, 693-9, 717-20(1922).—R. discusses vitamins under the following captions: notions concerning supplementary factors and their action, classification of these factors, their principal characteristics, their origin, quantities of vitamins in different foods, tests for the detection of vitamins, scientific theories concerning vitamins, and the pharmaceutical applications of vitamins. A bibliography of 33 references is appended.

A. G. DUMÉZ

The proteolytic enzymes of the spleen. S. G. HEDIN. *J. Biol. Chem.* **54**, 177-202 (1922).—100 g. minced ox spleen were mixed with 300 g. H_2O , 2.25 cc. 20% HOAc $CHCl_3$ and PhMe and kept at 37° for 24 hrs. The mixt. was filtered (filtrate A) and the residue was mixed with a solu. of 20 g. casein in 500 cc. 0.02 N NaOH, $CHCl_3$ and PhMe and again kept at 37° for 24 hrs. The mixt. was then filtered (filtrate B) and the residue was washed and then extd. with 5% NaCl at 37° for 24 hrs. The filtrate was treated with 30 g. $(NH_4)_2SO_4$ per 100 cc. and the ppt. obtained was filtered out and dialyzed. The protein ppt. was filtered out, dissolved in as little NaOH solu. as possible, filtered and called solu. C. Filtrate A contained varying quantities of (1) α -protease, acting upon spleen substance and upon casein in an alk. medium (p_H 8.8); (2) β -protease, acting upon spleen substance and upon casein in a weakly acid medium (p_H about 5.4) and (3) erepsin, not acting upon casein but upon Witte's peptone, most actively at p_H 7.5 to 8.5. Filtrate B contained chiefly β -protease and erepsin and solu. C, chiefly α -protease. Expts. described in detail indicate that the enzymes of the spleen lost a large part of their activity if the spleen was kept 24 hrs. in an alk., neutral or slightly acid (p_H 6.5) reaction, but retained their activity at p_H 5.2 and, after 24 hrs. at this reaction, were not destroyed by subsequent alkalization. But if first kept at a more alk. reaction, subsequent acidification did not reactivate the enzymes. Pig spleen resembled ox spleen but only 1 cc. of 20% HOAc was added to the mixt. of 100 g. spleen and 300 cc. H_2O because, although some acid was needed to prevent destruction of the enzymes, more than 1 cc. was slightly injurious. Horse spleen resembled ox spleen but the α -protease was more active at p_H 9.31 and β -protease at p_H 4.93. I. GREENWALD

What limits the form and form variations of mammalian erythrocytes? J. RUNNSTRÖM. *Arch. Entwickl. Organ.* **50**, 391-409 (1922).—The surface of erythrocytes is not an equil. form. Special differentiations must exist which oppose the surface relaxation. In corpuscles from horse blood, structures were observed which are explained as isolated strengthening bands at the border of the corpuscles. Other observations also indicate a reinforced border. This border, because of its tension, produces the biconcave form of the red cells. In Ringer solu., the red cells assume a spherical (crenate) form when influenced either by a positive or negative elec. charge. Certain isotonic solns. (especially KSCN) produce this form even in an uncharged medium. The appearance of bell-shaped corpuscles indicates that there is a decrease in the surface apparently conditioned by the increase in surface tension. The bell shape appears chiefly in corpuscles of low suspension stability. The red cells possess a colorless envelope. Certain changes of the colloidal state of the corpuscles are attributed to the changed relations between the lipoids and the proteins.

CHAS. H. RICHARDSON

The isolation of the thyroid hormones. I. B. ROMEIS. *Arch. Entwickl. Organ.* **50**, 410-67 (1922).—A thyroid ext., freed of protein with absolute alc. at a neutral reaction, produces acceleration of development in tadpoles of *Rana temporaria* but not the increase in catabolism observed when fresh thyroid tissue is fed. It is doubtful whether the so-called acceleration of development is specific for this organ. The protein pptd. by the 1st alc. pptn. exerts a strong increase in catabolism, restriction of growth and acceleration of development. The petroleum ether-sol. part of the alc. ext. does not accelerate development. By extg. fresh thyroid tissue with 50% alc., acidifying with AcOH and pptg. twice with 96% alc. an alc.-sol., protein-free fraction is obtained which increases catabolism, restricts growth and accelerates development in tadpoles; the protein substances pptd. with AcOH also produce these effects. This alc. ext. is not sol. in petroleum ether. It contains I. The alc.-extd. fraction is largely sol. in acetone. On sepg. the acetone ext. with C_6H_6 , toluene or $CHCl_3$, the active substance fails to pass into these solvents. Et_2O is not an effective solvent for the active substance in aq. soln.; it is more easily dissolved by Et_2O from an alc. soln. If this ext. is dried and taken

up with H_2O , the active substance remains in the residue. The active material is pptd. from a protein-free ext. by phosphotungstic acid in a H_2SO_4 soln.; the filtrate does not contain the active substance. When freed from the phosphotungstic acid ppt. with $Ba(OH)_2$, it is sol. in 90% alc. and free from I. By repeated soln. in 90% alc. a small amt. of a crystallizable substance was obtained from the weak H_2SO_4 soln. which *produced typical thyroid effects in tadpoles but was free from I*, thus differing from Kendall's thyroxin (C. A. 13, 2538). The active substance is pptd. by $HgCl_2$ in neutral soln. It is adsorbed from an aq. thyroid ext. along with the proteins by Al silicate in acid soln. It is further adsorbed from a protein-free ext. by both Al silicate and animal charcoal. From the Al silicate it is extd. with NaOH or NH_4OH ; in NaOH soln. it is not dialyzable through a collodion membrane. The ext. prepd. in this way is free from proteins, albumoses and peptones but contains I. On neutralization or acidification an active ppt. is obtained. KIO_3 , KI, $NaIO_3$, NaI and Lugol reagent in dilns. of 1-50,000 to 1-500,000 failed to accelerate development or restrict growth of tadpoles. Diiodotyrosine in small amts. (20-40 mg.) produces effects in tadpoles similar to thyroid feeding and iodothylin administration. Diiodotyramine, however, is not active. The activity here depends on the existence of the $COOH$ group; when the NH_2 group is substituted, activity is lost or greatly reduced. These expts. show that the specific activity of the thyroid gland depends upon a protein-free substance which is active without the presence of I, although I in some unknown combination doubtless increases its activity. It is S-free and gives no Millon reaction. Some active preps. lacked tryptophan, although Kendall's thyroxin is known to be a tryptophan deriv. It is not known whether the substance isolated corresponds to the hormone secreted *in vivo*, nor whether the results obtained with tadpoles will apply to the higher vertebrates.

CHAS. H. RICHARDSON

Oxyproteic acids. S. EDLBACHER. *Z. physiol. Chem.* 121, 164(1922); cf. C. A. 16, 3490.—The compd. previously reported appears to be acetylphenylhydrazine instead of the osazone of a tetrose.

R. L. STEHLE

The inactivation of saccharase by small amounts of silver salts. H. v. EULER AND KARL MYRDAËK. *Z. physiol. Chem.* 121, 177-82(1922); cf. C. A. 15, 1538.—Euler and Svanberg found the deleterious action of $AgNO_3$ on saccharase action to be directly proportional to its concn. E. and M. now report that this relation holds only for strong enzyme concns. With weak solns. the effect is the same as that observed with $HgCl_2$.

R. L. STEHLE

Chymosin and pepsin action. VII. Further researches on the purification of the gastric enzymes. OLOF HAMMARSTEN. *Z. physiol. Chem.* 121, 240-60(1922); cf. C. A. 14, 3254.—Starting with his crude enzyme prepn. from swine, H. has purified it further by removing NaCl and some other sol. constituents by 3 preliminary extns. with H_2O , (using about 100 cc. H_2O for each 3 g. of crude enzyme), effecting the sepsns. by means of the centrifuge, followed by a no. of similar extns. or a single extn. with a larger vol. of H_2O . The enzyme solns. obtained are about as active as Pekelharig's pepsin when compared on the basis of solid content, and keep for weeks. When such a soln. was compared with a soln. of Pekelharig's pepsin it was found that the ratio of the two with regard to pepsin action was 1:1.17, while for rennin action it was 2:1. Pekelharig's prepn. also showed no rennin action at 38° while H.'s prepn. was very active. **VIII. The different susceptibilities of the gastric enzymes of the calf and pig toward the action of alkali.** OLOF HAMMARSTEN. *Ibid.* 261-82.—H. finds that the chymosin of the pig as well as the pepsin is much more susceptible to alkali than the corresponding enzymes of the calf. Since the expts. of Michaelis and Rothstein, C. A. 14, 3429, were performed with the enzymes of the pig they do not militate against H.'s contention that in the calf the digestion of protein and the coagulation of milk are due to sep. enzymes.

R. L. STEHLE

Keratin. I. A. HEIDUSCHKA AND E. KOMM. *Z. physiol. Chem.* 121, 221-30 (1922).—The fusion temps. of keratin heated in bomb tubes alone and together with H_2O and concd. NH_3 were detd.; they were about 225-30°, 200° and 208°, resp. When heated *in vacuo* or at atm. pressure nothing happens below 250°; fusion then occurs and distn. begins.

R. L. STEHLÉ

Remarks on the work of E. Knaff-Lentz: "Blood saccharase and the antigenic properties of yeast saccharase." A further contribution to the question of the appearance of saccharase in the blood plasma after parenteral administration of sucrose. EMIL ABDERHALDEN. *Z. physiol. Chem.* 121, 233-7 (1922); cf. *C. A.* 16, 2490.—A. suspects that K. overlooked the possibility of mutarotation. A. has performed additional expts. and observed a change in rotation as well as in reducing power. Such expts. succeed in only a small porportion of cases.

R. L. STEHLÉ

Adrenal studies. HANS KUTSCHERA-AICHBERGEN. *Frankfurter Z. Path.* 28, 262-94 (1922).—Adrenaline reduces ammoniacal $AgNO_3$ in the tissues as it does *in vitro*; this reaction is used as a microchem. test for adrenaline. It is secreted in a dissolved condition by the adrenal marrow, and it may sometimes be demonstrated in the cortex capillaries. The adrenal has a double venous supply which is regulated to control the flow of adrenaline by the muscular app. of the medulla veins. The capsular veins of the left adrenal communicate directly with the portal and pancreatic veins, which may be of importance in relation to sugar metabolism. The chromaffin substance exhibits the character of an emulsion colloid, and may represent the ferment which produces the optically active adrenaline.

H. G. WELLS

Structure and significance of the phosphatides. P. A. LEVENE AND I. P. ROLF. *Physiol. Rev.* 1, 327-93 (1921).—An extensive critical review with full bibliography, discussing only the well defined phosphatides, namely, lecithin, cephalin and sphingomyelin. Curin is a mixt. of decompn. products of lecithin and cephalin. Recent progress in this field has been aided by the production of hydrogenated phosphatides which can be crystd. The graphic formulas of these substances are given on the basis of the best existing evidence. The physical, chemical behavior and the biol. aspects of the phosphatides receive particular consideration.

H. G. WELLS

Surface tension of serum. IV. Action of temperature. P. Lecomte du NOÛY. *J. Exptl. Med.* 36, 547-58 (1922); cf. *C. A.* 16, 1599.—The surface tension of pure serum, heated at 55°, decreases progressively and regularly until the serum coagulates. A drop of 8.2 dynes was observed in 168 hrs. The mean drop was 5.7 dynes in 120 hrs. and 4 dynes in 96 hrs. The initial surface tension of solns. of serum at the concns. 10^{-1} up to 10^{-4} is practically not affected by heat, but the time-drop in 2 hrs. is modified. Each serum seems to react in its own particular way as far as the time-drop is concerned. The concn. 10^{-4} seems to correspond to a state of greater instability than lower dilns. and confirms the hypothesis of the existence of a monomol. layer at that concn. which was assumed on the basis of the existence of a max. drop at 10^{-4} .

C. J. WESR

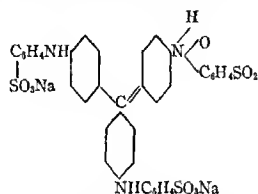
B—METHODS AND APPARATUS

STANLEY R. BENEDICT

The significance of the decomposition of the blood pigment in the intestines to porphyrin for the demonstration of occult blood in the feces. I. SNAPPER AND J. J. DALMEIER. *Deut. med. Wochschr.* 47, 985-6 (1921).—Feces are triturated with acetone; the filter residue is pressed out and the dried substance is treated with a soln. contg. 1 part glacial $AcOH$ and 3 parts $EtOAc$. To a part of the filtrate are added: pyridine $1/4$ of its vol., and 2 drops $(NH_4)_2S$. In the presence of hemochromogen the characteristic spectrum band (on border between yellow and green) is obtained. Another part of the filtrate may show the spectrum of acid hematin, chlorophyll or alk. porphyrin.

On addn. of $\frac{1}{4}$ the vol. 10% HCl and a small amt. of ether, after shaking, the ether contains the chlorophyll and hematin, and the watery soln. gives in the spectroscope the two bands characteristic for acid porphyrin. Chlorophyll is not decomposed in the human intestine to phyloporphyrin. The demonstration of porphyrin in the feces may be of clinical value since in a no. of cases it was shown that all the blood was in the form of porphyrin and could not be demonstrated otherwise. Its absence in the presence of occult blood speaks against malignancy. S. AMBERG

A new albumin reaction. A. M. HIBMA. *Deut. med. Wochschr.* 47, 272(1921).—Waterblue (Na salt of a dye acid) is the dye contained in the ink made by Van Gimbom.



To 20 cc. urine about 1 cc. 10% AcOH is added and 6-8 drops Gimbom's fox ink. If little albumin is present, the urine is heated, when a flocculent ppt. occurs. The reaction shows 0.005 pts. protein per 1000. The reaction is due to the liberation of the free dye acid which then combines with the protein. S. AMBERG

A new simple method for the determination of hydrochloric acid in stomach contents. L. v. FRIEDRICH. *Deut. med. Wochschr.* 47, 1258(1921).—The rather rough method is based on comparison of the blue color produced by a drop of stomach content, free from mucous, on Congo paper with a standard color scale. S. AMBERG

Method of blood sugar determination. R. OFFENBACHER AND A. HAHN. *Deut. med. Wochschr.* 27, 1419-20(1921).—Whole blood must be used for blood sugar detn. S. AMBERG

A new method for the quantitative determination of calcium in blood. R. WEISS. *Deut. med. Wochschr.* 47, 1298(1921).—Description of a small special titration app., in which a definite amt. of serum is treated with a definite amt. of $(\text{NH}_4)_2(\text{COO})_2$ soln. and the ppt. washed. H_2SO_4 is also added to a mark and then 0.01 M KMnO_4 until a red color remains for 2 mins. A scale on the instrument gives the amt. of Ca per 100 cc. serum. S. AMBERG

The colorimetric estimation of cystine in urine. J. M. LOONEY. *J. Biol. Chem.* 54, 171-75(1922); cf. FOLIN and LOONEY, *C. A.* 16, 1790.— Na_2SO_3 has no effect on the color produced by the interaction of uric acid, Folin-Denis uric acid reagent and Na_2CO_3 . With normal human urine, the addn. of Na_2SO_3 intensifies the color. This effect is believed to be due to the presence of cystine, apparently in amts. of from 0 to 10, av. 4, mg. per 100 cc. The standard cystine soln. contains 2 mg. per cc. in 5% H_2SO_4 . Into a 100-cc. volumetric flask, measure 1 cc. standard, 20 cc. satd. Na_2CO_3 , 10 cc. 20% Na_2SO_3 and 1 cc. 20% Li_2SO_4 . Into another flask, measure from 1 to 10 cc. urine and the reagents, and into a third flask, measure the same amt. of urine and the reagents, omitting the Na_2SO_3 . To each flask add 3 cc. Folin-Denis reagent, mix, let stand 5 min., dil. to 100 cc. and compare in colorimeter with standard set at 20 mm., within 8 min. after the addn. of the reagent. The amt. of cystine is calcd. from the difference indicated in cystine content, with and without Na_2SO_3 . Cystine pptd. in the urine is centrifuged out, dissolved in 5% H_2SO_4 and analyzed separately. Albumin is removed by adding 5 cc. 20% CCl_3COOH to 50 cc. urine, dilg. to 100 cc. and filtering. The filtrate is analyzed in the usual manner. I. GREENWALD

A method for the purification of picric acid for creatinine determinations. S. R. BENEDICT. *J. Biol. Chem.* **54**, 239-41(1922).—400 g. moist (10% H_2O) com. picric acid and 1 l. C_6H_6 are heated in a flask on an elec. plate until all the picric acid has dissolved. The mixt. is filtered hot through a paper moistened with C_6H_6 , leaving the H_2O and most of the insol. material in the flask. The filtrate is heated to redissolve any picric acid that may have crystd. and is then allowed to stand quietly overnight. The C_6H_6 soln. is decanted and the crystals of picric acid are washed twice with 75 cc. portions of C_6H_6 , drained and dried in the air or at 80° . A very good product is obtained. I. G.

The tryptophan content of some proteins. C. E. MAY AND E. R. ROSE. *J. Biol. Chem.* **54**, 213-6(1922).—0.05 and 0.1 g. portions of the proteins were added to 100 cc. 1:1 HCl contg. 1 cc. 5% *p*-dimethylaminobenzaldehyde in 10% H_2SO_4 and kept at 35° for 24 hrs. and then at room temp. for 40 hrs. The colors were then compared in a colorimeter with that of the standard, which was prepd. from 0.1 g. casein by the same method. Assuming the tryptophan content of the casein to be 1.5%, that of lactalbumin was 2.4, gliadin 1.05, glutenin 1.80, edestin 1.5, glycisin 1.65, ovovitellin 1.74, egg albumin 1.11, phaseolin 0.80, maize gluten 1.08, vetch legumin 1.05%, zein and gelatin 0.00. Cf. Folin and Looney, *C. A.* **16**, 1790. I. GREENWALD

The estimation of formic acid in urine. E. M. BENEDICT AND G. A. HARROP. *J. Biol. Chem.* **54**, 443-50(1922).—Dil. 100 cc. urine with 500-600 cc. H_2O , add 100 cc. 20% $CuSO_4$ and then a 10% suspension of $Ca(OH)_2$ until alk. but avoid an excess. Dil. to 1000 cc., mix and filter after 15 to 30 min. To 600 cc. filtrate add 1 to 2 cc. 85% H_3PO_4 and distil in a current of steam, reducing the vol. to 50 to 75 cc. and continuing distn. until 2 l. have been collected. The distillate is kept alk. to phenolphthalein by the addn. of 0.1 *N* NaOH as required and is then evapd. to dryness on a H_2O -bath. It is then treated with 100 cc. H_2O , filtered and an aliquot of 90 cc. is measured into a 250 cc. conical flask and acidified with 0.1 *N* HCl. 10 cc. of soln. contg. 200 g. $HgCl_2$, 80 g. NaCl and 300 g. NaOAc per l. are added; a stopper carrying an air condenser is inserted and the flask is immersed in boiling H_2O for 1 hr. After cooling, the $HgCl_2$ is filtered off on a Gooch crucible, washed with 100 cc. cold 5% HCl, E_2O , Et_2O and is then dried 1 hr. at 105° and weighed. The amt. found in a blank is subtracted. The calcn. is obvious. There was no increase in the formic acid of the urine in diabetic or starvation acidosis but it was increased in exptl. MeOH poisoning in a dog. I. G.

An apparatus for the determination of urea in small portions of blood and in organic secretions. ALEXANDER SZILL. *Deut. med. Wochschr.* **48**, 1278-80(1922).—An app. is described in detail with which the urea content of 1-1.5 cc. of blood can be detd. gasometrically. Protein-contg. liquids are freed from protein with CCl_3CO_2H . The liquid so obtained is treated with a soln. of NaBrO. The nitrogen evolved from the urea is measured in a capillary pipet with 0.001 cc. graduations. The nitrogen evolved does not come exclusively from urea; but the detns. are sufficiently accurate for clinical purposes. The method and app. are recommended for clinical use because of the speed with which detns. can be made and the small vol. of test liquid required.

MILTON HANKE

The determination of indican in blood serum. J. SNAPPER AND W. J. VAN BOMMEL VAN VLOTEN. *Klin. Wochschr.* **1**, 718-21(1922).—Free the serum from protein by the addition of an equal vol. of 20% CCl_3CO_2H . Dil. 2.5 cc. of the filtrate with water to 10 cc. Add 1 cc. of a 5% alc. soln. of thymol and 10 cc. of Obermayer reagent. Allow 20 min. for the reaction to go to completion and then ext. with 2 cc. of $CHCl_3$. A pale rose color is obtained with indican-contg. sera. Normal sera give a negative reaction. In cases of renal insufficiency, with indican retention, positive tests are obtained. Sera that have been deproteinized with alc. give lower values than those in which CCl_3CO_2H has been used. The color in this case is blue-violet. CCl_3CO_2H enters into the

color-producing reaction in some undetd. way. The thymol soln. must be added to the serum filtrate before the Obermayer reagent to obtain a max. of color. The patients must not receive iodides prior to the detn. Iodides give rise to a red to violet color with Obermayer reagent (liberation of iodine). Only fresh filtrates should be used; old filtrates give less intense colors.

MILTON HANKE

Methods used in testing liver function. K. RETZLAFF. *Klin. Wochschr.* 1, 850-5 (1922).—A review of the modern methods and what appears to be a good bibliography.

MILTON HANKE

A new micromethod for the separate estimation of acetone and β -hydroxybutyric acid in the urine. ALFRED LUBLIN. *Klin. Wochschr.* 1, 894-5 (1922).—From 0.5 to 1.0 cc. of urine are mixed with 25 cc. of water, 1 cc. of 10% AcOH and a little talcum, in a 50 cc. micro-Kjeldahl flask. The mixt. is boiled, the vapor condensed in a water jacketed condenser and the distillate collected in a 200-cc. Erlenmeyer flask to which has been added 10 cc. of a 0.01 *N* I soln., 5 cc. of a 25% NaOH and 40 cc. of water. The distn. is interrupted at the end of 10 mins. This first distn. drives off all the preformed acetone, as well as the acetone that arises from acetoacetic acid on heating. The receiving flask is now replaced by one contg. a fresh portion of I, alkali, etc., as above, excepting that 15 cc. of 0.01 *N* I should be used. To the reaction mixt. 20 cc. of a soln. contg. 2.0 g. $K_2Cr_2O_7$ and 20 cc. of H_2SO_4 in 80 cc. of H_2O are now added, drop by drop. This converts the β -hydroxybutyric acid into acetone which is then distd. off and collected as in the first case. The I, not converted into iodoform by the acetone, is estd. by titrating back with 0.01 *N* $Na_2S_2O_3$ after the addn. of 5.0 cc. of a 25% H_2SO_4 soln. The entire process can be carried out in 25 mins.

MILTON HANKE

Explanation of the Giemsa stain. P. G. UNNA. *Centr. Bakt. Parasitenk.* 1 Abt. 88, 159-64 (1922).—An attempt to explain the metachromic effect of the Giemsa stain as due to the action of the "bausteine," of methylene blue. Giemsa's stain produces essentially the same effect that is obtained in U.'s polychrome methylene blue. The role of eosin in the Giemsa stain seems to be that of a mordant. J. H. L.

Ammonia estimation in blood serum. HERMAN STRAUSS. *Zentr. inn. Med.* 43, 26-8 (1922).—The method used is that of Hahn and Kootz (*C. A.* 14, 3255) which consists of distg. off the NH_3 at 70-75° after the addition of not excessive amts. of alkali. The normal value for blood NH_3 is between 1 and 2 mg. per 100 cc. High values are found in diabetic acidosis, nephritis, uremia and pyelitis.

JULIAN H. LEWIS

Blood detection with pyramidone. ANTON FORTWAENGLER. *Zentr. inn. Med.* 43, 313-17 (1922).—The following solns. are used: (1) pyranidone 5, 90% EtOH 100; (2) glacial AcOH 25, distd. H_2O 25; (3) 3% H_2O_2 . To 2-3 cc. of the soln. to be tested add 6-8 drops of 50% AcOH and 2 cc. of 5% pyramidone soln. in 90% alc. Add 6-8 drops 3% H_2O_2 , shake and allow to stand. A lilac color is produced in positive tests. The H_2O_2 soln. can be added so as to form a ring. This test is more sensitive than the guaiac test and is not of the extreme sensitiveness possessed by the benzidine test. Feces must be first extd. with neutral ether. One source of error is that pus gives a positive test. In this case, the specimen should be boiled after slightly acidifying with acetic acid. The filtered soln. can then be safely used.

JULIAN H. LEWIS

Shaking machine for large amounts of fluids. HARTWIG FRANZEN. *Z. physiol. Chem.* 122, 86-7 (1922).—A seesaw device operated by a $1/10$ h.-p. motor. Containers up to 24 l. may be accommodated.

R. L. S.

Mechanism of the Straub biologic test for morphine. W. J. R. HEINEKAMP. *J. Pharmacol.* 20, 107-13 (1922).—The Straub biologic test (*Deut. med. Wochschr.* 37, 1462) is due to the direct stimulation of the cord. It is not specific for morphine but is indicative of spinal cord stimulation.

C. J. WEST

C—BACTERIOLOGY

A. K. BALLS

The disinfection of tuberculous sputum. P. UHLENHUTH AND K. W. JÖRTEN. *Arch. Hyg.* 91, 85-98(1922).—The best results were obtained with a prepn. called alkalyzol. Practically, 2 vols. of a 5% soln. should be mixed with 1 vol. of sputum and allowed to act for at least 4 hrs.

JULIAN H. LEWIS

The application of the Arndt-Schulz biological law to the action of bactericides. PAUL HOFMANN. *Arch. Hyg.* 91, 231-44(1922).—The Arndt-Schulz biol. law proposes that every manifestation of life is the result of a stimulation. The same stimulation may initiate, accelerate, inhibit or destroy vital processes according to the force of its action. This law is applied to the action of various bactericidal substances on different bacteria. It is found that some bactericides that kill in high concns. will accelerate the growth of bacteria in low concns. This is not true for all bactericides, because when the concn. is below that of inhibitive action some become indifferent.

JULIAN H. LEWIS

The significance of the capsule for the virulence of *Sarcina tetragena*. KARL MAYR. *Arch. Hyg.* 91, 209-16(1922).—Encapsulated *Sarcina tetragena* could be made to lose their capsule by repeated transfers at short intervals and by heating $\frac{1}{2}$ hr. at 52-53°. The non-encapsulated form is energetically phagocytosed and is avirulent for animals. The encapsulated form is not phagocytosed and is virulent. The capsule is a protection for the *S. tetragena* just as it is for the anthrax bacillus. J. H. LEWIS

The influence of intravenous injection of foreign protein on the bactericidal action of serum. ORRO PFEILER. *Arch. Hyg.* 91, 217-30(1922).—No effect was found in normal horses and rabbits.

JULIAN H. LEWIS

A substitute for the Lugol solution in the Gram stain. K. VIERLING. *Centr. Bakt. Parasitenk.*, I Abt. 83, 169-70(1922).—(1) To 100 cc. aniline-methyl violet (1 l. H₂O is shaken with 30 cc. aniline oil and filtered; 100 cc. concd. alc. soln. of methyl violet is added) add 4 cc. 1% night blue soln. Stain the prepn. $\frac{1}{2}$ min. and wash with H₂O. (2) Drain off H₂O and add NH₄ picrate (3 g. picric acid dissolved in 200 cc. water and 2.2 cc. 10% NH₄OH added) for $\frac{1}{2}$ min. Dry with filter paper. Decolorize with 90% alc. 2-10 sec. Remove alc. and counterstain with a mixt. of rhodamine and neutral red (0.2 g. of each in 100 cc. H₂O) or with dil. carbofuchsin. Gram-positive bacteria are blue-violet and Gram-negative ones are red.

JULIAN H. LEWIS

The use of physical methods for investigations of bacterial growth. P. A. HOFFER. *Centr. Bakt. Parasitenk.*, I Abt. 88, 171-4(1922).—The interferometer, the refractometer and the Tyndall phenomenon are suggested for use in studying the changes in culture media which result from bacterial growth.

JULIAN H. LEWIS

A new modification of the stain for spirochetes. V. RENE. *Centr. Bakt. Parasitenk.*, I Abt. 88, 174-5(1922).—Two solns. are needed: (1) tannic acid 5 g., acetic acid 2 cc., 4% formalin 5 cc., distd. H₂O 40 cc., 96% alc. 60 cc.; (2) AgNO₃ 5 g., distd. H₂O 100 cc. Prep. thin smears, dry in air and cover with soln. (1). After a brief warming in the flame allow the alc. vapor to ignite. Keep the prepn. from being burned by stirring the fluid with a small rod. Wash in water to which a few drops of NH₄OH are added (10-50 drops in 1 l.). Cover with soln. (2) and warm slightly. Wash in distd. H₂O and then dry.

JULIAN H. LEWIS

Acid agglutination of the Weill-Felix X strain of the proteus bacillus. Z. BIEN. *Centr. Bakt. Parasitenk.*, I Abt. 88, 177-80(1922).—This strain is agglutinated with acid between p_H 2 and 4. The optimum reaction is p_H 3. Many proteus strains which have no relation to typhus are not agglutinated with p_H 3 as an optimum. The H and O forms of the X strain of proteus bacilli act differently to acids, as the O form is not agglutinated by acids. The H form is pptd. by 33% alc. while the O form is not.

JULIAN H. LEWIS

The vaccine-fastness of staphylococci and its relation to staphylolysin. TOMOSUKU MAYEDA. *Centr. Bakt. Parasitenk.*, I Abt. 88, 222-9(1922).—Ten strains of virulent staphylococci which could withstand vaccine (iso-octylhydrocupreine dihydrochloride in a max. concn. of 1:2000 to 1:10000 could, by repeated transfers from such a soln., be made to withstand this substance in a concn. of 1:5000 to 1:300. The max. concn. of vaccine in which staphylococci can grow varies among strains and a given strain may show a decrease in its resistance without a cause. The change in resistance acquired by transfer is limited with many strains to vaccine. After several passages through vaccine there is a lowered ability to form staphylolysin and to liquefy gelatin. The increased resistance to vaccine is not easily lost by growing on plain agar.

JULIAN H. LEWIS

An oxygen indicator for the growth of anaerobic bacteria. M. VAN RIENSDIJK. *Centr. Bakt. Parasitenk.*, I Abt. 88, 229-52(1922).—See C. A. 16, 3920. J. H. L.

The chemical composition of the polar bodies of diphtheria bacilli. J. SCHUMACHER. *Centr. Bakt. Parasitenk.*, I Abt. 88, 362-6(1922).—The polar bodies of diphtheria bacilli consist of free nucleic acid. It is not known whether also bound nucleic acid occurs in these organisms. The methylene blue-phosphin of the Neisser stain colors the polar bodies green and the bacilli yellow. The methylene blue-quinine-eosin method stains the polar bodies blue and the bacilli red. These stains are not sp. for diphtheria bacilli but are only histochem. reagents which act on free nucleic acid.

JULIAN H. LEWIS

The cultural and serological differences between *B. breslaviensis* and paratyphoid B bacilli. LEO OLTZKI. *Centr. Bakt. Parasitenk.*, I Abt. 88, 460-7(1922).—Of 13 cases with enteritis, the organism isolated could be identified serologically as paratyphoid B in 4 cases. In 5 cases the organism was definitely the *B. breslaviensis*. In the remaining 4 cases the organism isolated could not be identified serologically as *B. breslaviensis* or paratyphoid B as it was agglutinated in high titer by both antisera.

JULIAN H. LEWIS

A new biological reaction for cholera vibrio. II. KODAMA AND H. TAKEDA. *Centr. Bakt. Parasitenk.*, I Abt. 88, 513-8(1922).—The reaction depends on the presence of a diastatic enzymes in cholera vibriones. The culture medium used is prep'd. by adding 1 g. peptone, 0.5 g. potato starch and 2 cc. of 10% soda soln. to 100 cc. H₂O. It is tubed in 5-cc. lots and sterilized on 3 successive days. After inoculation and incubation for 24 hrs. 5 cc. of Lugol's soln. are added. The amt. of starch that has been digested is indicated by the color which results. A study of various pathogenic and nonpathogenic organisms shows that cholera vibriones digest the starch most. Organisms similar to cholera vibriones digest starch less; anthrax hay and coli bacilli digest it very weakly and other organisms not at all. Stools suspected of contg. cholera vibriones are incubated 7-24 hrs. in the medium and then the Lugol's soln. is added. If a yellow color is produced the presence of cholera can be presumed.

JULIAN H. LEWIS

The serum fastness of typhoid bacilli. HIDEZO TOYODA. *Centr. Bakt. Parasitenk.*, I Abt. 88, 539-48(1922).—Serum-fast typhoid bacilli absorb both homologous and heterologous agglutinins and bacteriolytins very slowly. They are, however, much better antigens than nonserum-fast organisms. Serum fastness is due to an increased physical resistance and not to a change in the construction of the receptors. J. H. L.

Glycogen in culture media. WILHELM ROTHER. *Centr. Bakt. Parasitenk.*, I Abt. 88, 560-2(1922).—Cloudiness in culture media which is not cleared by boiling with proteins may be due to glycogen. This may be removed by adding saliva, pancreatin, blood serum or ascitic fluid and incubating.

JULIAN H. LEWIS

The growth-inhibiting action of bouillon cultures. K. HAJOS. *Centr. Bakt. Parasitenk.*, I Abt. 88, 583-5(1922).—Bouillon cultures of the colon-typhoid organisms were repeatedly inoculated and centrifuged bacteria-free until the organisms no longer grew in the cultures. This inhibitive action was not sp. in that it inhibited closely

related bacteria. It is not bactericidal and when inoculated growth is not inhibited after 72 hrs. The inhibiting cultures are not toxic for guinea pigs. They are completely regenerated when 2 parts of fresh bouillon are added. The p_H of these exhausted cultures varied for each organism and ranged from 4.5 to 8.0. The inhibitive action is not influenced by heating to 100°. This action of exhausted cultures is due to the presence of some thermostable metabolic product and is not related to the d'Herelle phenomenon.

JULIAN H. LEWIS

Fermentation agglutination. B. KLEIN. *Centr. Bakt. Parasitenk.*, I Abt. 88, 589-593(1922).—*B. coli*, *B. paracoli*, *B. typhosus*, *B. paratyphosus* B, *B. enteritidis*, staphylococci, *B. proteus* 19X, *B. dysenteriae* and *Vibrio cholerae* are agglutinated in 1-2 days in dextrose broth cultures. This agglutination is const. and is due to the acid formed in fermentation. While *B. coli* and *B. dysenteriae* are in most cases not agglutinated by acids with the method of Michaelis they are always in dextrose broth cultures. Agglutination occurs not only in dextrose broth cultures but also in levulose broth cultures.

JULIAN H. LEWIS

The decolorization of tubercle bacilli with sodium sulfite. J. VON BERGEN. *Centr. Bakt. Parasitenk.*, I Abt. 88, 598-602(1922).—The modified Ziehl-Neelsen stain as proposed by Konrich (*Deut. med. Wochschr.* 1920), in which decolorization is accomplished by means of a soln. of Na_2SO_3 , proved inferior to the original method. It was too slow and gave inconstant results.

JULIAN H. LEWIS

Serological classification of the nodule bacteria of leguminous plants. M. KLIMMER. *Centr. Bakt. Parasitenk.*, I Abt. 55, 281-3(1922).—The nodule bacteria from 18 species of leguminous plants are sepd. into 9 different classes by agglutinating and pptg. antisera.

JULIAN H. LEWIS

A blue-pigment-forming bacillus isolated from the air and its relation to the bacillus of blue milk. HERMANN MILHENSEN. *Centr. Bakt. Parasitenk.* II Abt. 56, 309-28 (1922).—This organism does not correspond completely with the *B. cyanogenus* isolated from blue milk or with any other blue-forming organism.

JULIAN H. LEWIS

Iron bacteria as inorgoxidants. S. WINOGRADSKY. *Centr. Bakt. Parasitenk.*, II Abt. 57, 1-21(1922).—The role of Fe in these bacteria is discussed. While the deposit of Fe is considered by some writers as purely mech., W. believes it is a vital process and that the bacteria belong to that class known as inorgoxidants. These bacteria obtain all their energy from the oxidation of inorg. substances. They possess little or no ability to attack org. substances which may, on the other hand, be harmful. CO_2 is the source of C.

JULIAN H. LEWIS

The comparative behavior of various acid-fast bacilli to extraction with ether-acetone mixtures. W. PFANNENSTIEL. *Z. Hyg. Infektionskrankh.* 95, 87-99(1922).—The extn. of tubercle bacilli with $CHCl_3$, xylene, ether, acetone and ether-acetone mixts. could not make tubercle bacilli non-acid fast without previous treatment by boiling, destruction by mech. force, or with acids and alkalis. The fat obtained in this way was very similar to beeswax. Both were acid-fast. The fats from a series of acid-fast bacilli of different origin gave little difference in their staining reaction. All strains when extd. 48 hrs. with ether, $CHCl_3$ and acetone retained their form and never completely lost their acid-fastness. The human, bovine and avian types did not lose any while the so-called saprophytic types lost most of their acid-fastness. The amt. of lipid that can be extd. from human tubercle bacilli varies between 2.85 and 11.9%; from the turtle bacillus it varies between 3.85 and 5.02%; from the avian bacillus it was 13.05%. The amt. of lipid from the butter bacillus varied from 2.68 to 10.17%, but when this organism was passed through the guinea pig 3 or 4 times the % varied between 9.44 and 15.4. The amt. of more or less acid-fast lipoidal substance lost by the organism upon extn. does not parallel the amt. of acid-fastness which they lose after extn.

JULIAN H. LEWIS

The testing of disinfectants. LUDVIG BITTER. *Z. Hyg. Infektionsk.* 95, 119-24 (1922).—The procedure is outlined which should be used in testing the efficacy of new disinfectants.

JULIAN H. LEWIS

The growth of tubercle bacilli in fluid mediums containing egg yolk. EDWARD BOECKER. *Z. Hyg. Infektionskrankh.* 95, 344-6 (1922).—The egg yolk medium for tubercle bacilli described by Besredka (*Ann. inst. Pasteur.* 35, no. 5, 1921), while not completely satisfactory, gives promise of being a good medium if modified as suggested by the author.

*JULIAN H. LEWIS

Adsorption disinfection. H. BECHHOLD AND R. REINER. *Z. Hyg. Infektionskrankh.* 96, 17-24 (1922).—The metal charcoals are preps. of finely divided charcoal on the surfaces of which are deposited by a reduction process one of the heavy metals (Cu, Ag, Au, etc.). These metal charcoals, because of their adsorptive capacities, are efficient disinfectants. Their disinfectant properties are lowered in the presence of insol. but indifferent finely divided substances, even though these indifferent substances have highly active surfaces. The combination of 2 insol. disinfectants produces a decrease in their action if the adsorptive surface remains const. or if the mass remains const. and the adsorptive surface is increased. Disinfectants with active surfaces and finely divided solid but insol. disinfectants inhibit each other.

JULIAN H. LEWIS

The mass of bacteria in testing disinfectants. BRUNO LANGE. *Z. Hyg. Infektionskrankh.* 96, 92-117 (1922).—Disinfectants tested with large nos. of bacteria or thick emulsions are inhibited in their action, probably because of adsorption processes.

JULIAN H. LEWIS

Clinical and serological characteristics of the Breslau paratyphoid B. HOLM AND F. H. LEWY. *Z. Hyg. Infektionskrankh.* 96, 288-97 (1922).—The paratyphoid B organisms isolated from 2 cases of meat poisoning in Breslau were serologically different from the paratyphoid B of Schottmüller. These 2 infections were characterized with a very rapid and severe onset.

JULIAN H. LEWIS

The influence of chemotherapeutic silver preparations on the bactericidal action of whole blood. HUGO KÄMMERER AND LUDWIG SCHARTZ. *Z. Hyg. Infektionskrankh.* 96, 298-316 (1922).—By adding Ag preps. to whole blood in concns. that are obtained in man by intravenous injection it is impossible to increase the bactericidal action of the blood. The known bactericidal actions of Ag preps. are inhibited because of adsorption by the corpuscular and colloidal constituents of the blood. An exception is fulmarin, a colloidal Ag prep. obtained by electrolysis. No evidence was obtained that bacteria are so injured by Ag preps. that they are more readily attacked by the physiological protective substances in the blood.

JULIAN H. LEWIS

Increased sensitivity of bacteria. ALFRED SCHNADEL. *Z. Hyg. Infektionskrankh.* 96, 351-86 (1922).—Pneumococci grown 24 hrs. in high concns. of optochin (1:500000) develop a fastness to this substance while those grown in low concns. (1:60,000,000 and higher) develop an increased sensitivity to optochin. The increased sensitivity was relatively sp. in that the organisms were not increased in sensitivity to phenol but were, to some extent, to drugs closely allied to optochin chemically. Pneumococci grown in various concns. of CH_3O developed changes in resistance to CH_3O at the extremes of concn. as with optochin. The increase in sensitivity to CH_3O was also exhibited to optochin but not to phenol. Staphylococci grown in low concns. of HgCl_2 showed an increased sensitivity to HgCl_2 and to AgNO_3 but not to phenol and optochin. The results with members of the dysentery and colon group were less striking. J. H. L.

Salteffects in bacterial growth. II. The growth of *Bacillus coli* in relation to hydrogen-ion concentration. J. M. SHERMAN AND G. E. HOLM. *J. Bact.* 7, 465-70 (1922).—The addition of 0.20 M concn. of NaCl in a peptone soln. widened the optimum pH range for *B. coli* and *B. alkaligenes* but not for other organisms tried. Without NaCl *B. coli*

failed to grow at a p_H of 4.8. With the above concn. of NaCl it grew rapidly. Na citrate markedly narrows the p_H limits.

JOHN T. MYERS

The properties of bacteriolytants. I. W. C. DAVISON. *J. Bact.* 7, 475-90(1922).—The filtrates of stools of infants suffering from bacillary dysentery (Flexner), acute intestinal indigestion, otitis media, and the need for regulation of feeding, were bacteriolytic for one or more of 27 strains of Flexner, Shiga and typhoid bacilli. This phenomenon is apparently non-specific. The action is more nearly complete in low concns. and at a p_H of 8.0 to 8.2. Saline and peptone water solns. were equally lysable. A concn. of 0.2 *N* NaOH destroyed bacteriolytant activity. Heating to 60° to 67° has no effect on a filtrate. Bacteriolytants were non-pathogenic for rabbits. II. *Ibid* 491-504.—The lytic principle in d'Herelle's phenomenon seems to be an enzyme. It is not trypsin. A small amt. of the lytic agent is contained in or produced by normal strains of Flexner bacilli which have been out of contact with the human body for years. It is possible that the amt. of the bacteriolytic enzyme produced by a culture can be increased by aging, growth in special media, or by contact with external secretions, tissue exts., etc. This enzyme not only dissolves organisms but favors the multiplication of bacteria which produce the enzyme. It is highly improbable that this phenomenon is a defense action against bacterial invasion.

JOHN T. MYERS

The action of various antiseptics on wounds infected with streptococcus. O. SCHIEMANN AND WRESCHNER. *Z. Hyg. Infektionskrankh.* 96, 424-41(1922).—Comparative expts. with many bactericidal substances as to their disinfectant action *in vitro* and in sterilizing streptococcus-infected wounds in animals lead to the conclusion that trypanlavine was the most active.

JULIAN H. LEWIS

Bactericidal action of certain vegetable essences in the liquid state. A. MOREL AND A. ROCHAUX. *Compt. rend. soc. biol.* 86, 933-4(1922).—The following essences were found to possess bactericidal action on meningococci, staphylococci, diphtheria bacilli and Eberth's bacillus: essence of thyme, citron, juniper and mint.

S. MORGULIS

The relation of vitamins to the growth of a streptococcus. S. H. AYERS AND C. S. MUDG. *J. Bact.* 7, 449-64(1922).—The effect of various exts. on the growth of a pathogenic streptococcus was tried. Autolyzed yeast ext. contained a growth-promoting substance, but water-sol. B did not appear to be the significant substance. Cabbage ext. promoted growth but a glucose soln. contg. the same amt. of sugar as the cabbage ext. gave the same results. Fats and oils, vegetable, animal and mineral, even in very small amts. stimulated the growth of the streptococcus. Either the growth-promoting property of fats and oils is not due to fat-sol. A or this vitamin is present in mineral oils, or the stimulation is due to different causes in the case of the vitamin contg. fats and oils and the mineral oils.

JOHN T. MYERS

Transparent milk as a bacteriological medium. J. H. BROWN AND P. E. HOWE. *J. Bact.* 7, 511-4(1922).—Fat-free milk may be transformed into a transparent medium by the addition of small amts. of various salts; 0.4% Na citrate is most suitable. Changes can be easily observed, and colorimetric p_H detns. made.

JOHN T. MYERS

The use of agar slants in detecting ammonia production and its relation to the reduction of nitrates. C. J. HUCKER AND W. A. WALL. *J. Bact.* 7, 515-8(1922).—The various chem. tests are applied to agar slant growths instead of to liquid cultures.

JOHN T. MYERS

American gentian violets. Report of Committee on Bacteriological Technic. H. J. CONN, *et al.* *J. Bact.* 7, 529-36(1922).—Samples of crystal violet, methyl violet 6B, and gentian violet made in America, can be used in the Gram technic. Cf. C. A. 16, 1802.

J. T. M.

Supposed transformation of the nitric enzyme in saprophytic species. S. WINOGRADSKY. *Compt. rend.* 175, 301-4(1922).—These bacteria, which are characterized

by their ability to oxidize inorg. substances, occupy an exceptional place among living organisms. Their respiration is not made at the expense of carbohydrate material with CO_2 as a product, but upon mineral substances capable of oxidation such as H_2S , S , FeO , NH_3 or HNO_3 , according to the function always narrowly specialized in the different sub-groups of these organisms. They are incapable of decomposing and utilizing org. material but develop in mediums purely mineral and can assimilate CO_2 . Org. substances, always present in natural mediums, if in small amts. do not hinder the specific process of oxidation, but in larger amts. render the nitrifying organisms, or enzymes, inactive until the excess is destroyed by the saprophytes of the soil. The varying explanations of the actions of the nitrifying organisms may often be referred to faulty technic and lack of suitable controls in the culture of these organisms. The work of Beijerinck is criticized from this point of view.

—L. W. RIGGS

The thermal death time of spores of *Clostridium botulinum*. E. C. DICKSON, GEORGINA S. BURKE, DOROTHY BECK, JEAN JOHNSTON AND HARRIET KING. *J. Am. Med. Assoc.* 79, 1239-40 (1922).—In open-tube tests of 40 strains of *C. botulinum*, heated at 100° , the survival time varied between thirty min. and 6 hrs. Some of the most resistant strains were Type A and some were Type B. From observations based on about 40 thousand tubes it appears that 95% of the spores are quickly destroyed, and that among the remaining 5% there are a few spores much more resistant than the others. There may be a very marked delay of germination of spores of *C. botulinum* after they have been heated. In the expts. some tubes remained apparently sterile after others had shown growth, but would eventually show vigorous growth with toxin formation. The longest delay thus far observed is 330 days. The causes of this delayed germination are not known. Spores in a culture aged 22 days were less resistant than those in a culture aged 66 days, but between 66 and 315 days the resistance was practically constant. The max. resistance exists when the medium is approx. neutral and rapidly decreases as the H-ion concn. approaches both the acid and alk. ranges. There is a much narrower zone of greater resistance at higher than at lower temps. Studies by sealed-tube technic showed no difference between HCl , AcOH , citric and lactic acids at the same H-ion concn. in their effects upon the resistance. The kind of medium in which the spores have grown does not seem to influence their heat resistance, but there is a variation in the heat resistance depending on the type of substratum in which they are heated. Spores heated in broth are more quickly destroyed than when heated in brain medium; and if a thin layer of oil is placed on the surface of the broth, there is a greatly increased survival after the heating process. In sealed tubes the survival time at 100° is less than that obtained in open tubes.

L. W. RIGGS

Botulinus toxin. J. BRONFENBRENNER. *Science* 56, 280-2 (1922); cf. C. A. 15, 3681.—In a previous paper it was stated that quantities of a soln. which contained only 3×10^{-13} exhibited all the specific properties of the original toxin and killed mice in 48 hrs. when injected intraperitoneally. This statement was questioned by Stehle on the ground that such a diln. would not furnish one molecule of toxin per cc. The expts. were carefully repeated with the following results: When 3×10^{-18} of the acidified culture filtrate of *B. botulinus* is injected intraperitoneally into mice of 17 to 21 g. wt. the animals die in 24 to 48 hrs., the typical incubation period, with all the symptoms of botulinus poisoning in mice. Animals receiving a protective injection of a homologous (type A) antitoxin invariably survive the injection of an amt. many millions of times greater than 3×10^{-13} of the active soln. Animals receiving large amts. of heterologous (type B) antitoxin are not protected against a single dose of 3×10^{-13} of the active toxin. The potency of the active toxin is destroyed by a very short exposure to heat at 80° . When the reaction of acidified toxin is brought back to neutral (before diln.), the resulting soln. has the titer of the original toxin. The reacidification and

reneutralization can be accomplished several times in succession with the result that acidification invariably increases the potency and neutralization returns it to the original titer. When 1 cc. of the original toxin has been distributed through a sufficiently large amt. of a diluent so that not every cc. of the diluent would be theoretically expected to contain one molecule of original toxin, the results of injection of such highly dild. toxin become irregular and apparently depend on the presence or absence of a molecule or small number of molecules of toxin in each portion injected. While not every filtrate yielded an equally potent product on acidification, the same filtrate consistently titrated as indicated, even though repeated tests were performed several days and weeks apart. It is difficult to reconcile the low mol. wt. and small number of molecules which must be present in the diln. used, with the results observed, and it is not explained why such a simple molecule as that which the active toxin appears to possess cannot pass the bacterial filters which are comparatively permeable to the original toxin. L. W. RIGGS

Occurrence of sulfate-reduction in the deep layers of the earth (KÜHR) 8. Study of the causation of "ropiness" in worts and beers (HAMPSHIRE) 16.

D—BOTANY

B. M. DUGGAR

A reversible increase of viscosity of living protoplasm with narcosis. F. WEBER. *Ber. botan. Ges.* 40, 212-16(1922).—Data are recorded showing the influence of varying concns. of Et_2O in H_2O on sections of epicotyls of *Phaseolus vulgaris*. The viscosity of the protoplasm was increased when 2.5% of Et_2O was used. This increase was reversible, the original viscosity being obtained after washing in H_2O for several hrs. The viscosity increase is not reversible after exposure of the plumule to 10% Et_2O . The details of the tests are given. Narcotics act not only on the plasma membrane but also on the endoplasm. F. C. COOK

Presence of cobalt and of nickel in plants. GABRIEL BERTRAND AND M. MOKRAG-NATZ. *Compt. rend.* 175, 458-60(1922).—The analytical methods have been improved so that not only Co and Ni but Zn and Cu can be detd. in 0.02 g. of soil. Analyses of the ash of 20 samples of mostly food vegetables showed that every sample contained Ni and all but oat and carrot contained Co. One kg. of material was used for the detn. of Co and Ni in the case of seeds, 2 kg. in the case of leaves or stalks. The proportion of Co in plants ranges between less than 0.02 mg. and 0.3 mg. per kg. of fresh material. The corresponding range for Ni was 0.01 in tomato to 2.0 in peas. As little as 0.005 mg. of Co will show crystals of cobaltinitrite. Even in the carrot the color reaction of Co with dimethylglyoxime and $(\text{NH}_4)_2\text{S}$ was obtained. L. W. RIGGS

Decomposition of kaolin by organisms. W. J. VERNADSKY. *Compt. rend.* 175, 450-2(1922).—J. Murray and R. Irvine (cf. *Proc. Roy. Soc. Edinburgh* 18, 245(1891)) showed that sea water did not contain SiO_2 in sufficient amt. to maintain the diatoms present. Murray suggested that the diatoms were able to decompose clay and utilize the silica thus liberated. It was proved that the diatom *Navicula* could flourish in water in which SiO_2 was absent but clay was present. V. sowed cultures of the *Nitzschia* diatom on colloidal clay of the compn. $\text{H}_2\text{Al}_2\text{Si}_2\text{O}_5 \cdot \text{H}_2\text{O}$, supplied with a nutritive medium from which SiO_2 was removed. The diatoms developed readily. The cultures were made in glass vessels coated internally with paraffin. Free $\text{Al}(\text{OH})_3$ was produced during the nutrition of the diatoms. With controls contg. no diatoms, $\text{Al}(\text{OH})_3$ was not formed. L. W. RIGGS

The chemical constituents of green plants. XIX. Occurrence of lactic and succinic acids in the leaves of the raspberry (*Rubus idaeus*). HARTWIG FRANZEN AND EMMI STERN. *Z. physiol. Chem.* 121, 195-220(1922).—The salt mass obtained from the aq. ext. of raspberry leaves after pptn. with Pb acetate consists almost wholly of

of lactic acid. The ether ext. of the filtrate from the salt mass consists largely of lactic acid together with small amts. of substances sol. in C_6H_6 , a little succinic acid, and some unsatd. acids. XX. The acids of the cherry (*Prunus avium*). HARTWIG FRANZEN AND FRITZ HELWERT. *Ibid* 122, 46-85(1922).—The principal acid of cherries is malic acid; traces of oxalic, succinic, citric, lactic and of unsatd. acids also are present.

R. L. STEHLÉ

Phycocerythrin in Myxophyceae. N. WILLIE. *Ber. botan. Ges.* 40, 188-92(1922).—The spectra of *Phormidium persicinum* and of *Rhodomenia palmata* are identical. In the former a true *Florideae*-phycocerythrin and not a *Schizophyceae*-phycocerythrin appears. The relation and origin of the coloring matter of these 2 algae are discussed.

F. C. COOK

Formation of anthocyanin under the influence of light in the scales of the bulbs of certain lilies. MARCHÉ, MIRANDÉ. *Compt. rend.* 175, 429-30(1922).—Scales detached from the bulbs of the white and Turks-cap lily and exposed to light for a few hrs. become intensely red by the formation of anthocyanin in their sub-epidermal layers. These pigmented scales produce at the expense of their substance bulbils furnished with roots. So long as they are not detached from the scale which carries them the bulbils keep fresh for several months and when placed in soil grow to a new plant. For the production of these bulbils it is necessary that the scales do not dry out. This condition is attained by the formation of anthocyanin, which, on account of its strong osmotic pressure, protects the scale against withering. In the absence of light the scales produce no anthocyanin and rapidly wither. The red coloring matter was extd. with alc. and tested with various reagents.

L. W. RIGGS

Role of respiration in the diminution of carbohydrates in leaves during autumnal yellowing. RAOUL COMBES and DENISE KOHLER. *Compt. rend.* 175, 400-9(1922).—Leaves of *Fagus siliatica* and of *Aesculus hippocastanum* collected at the beginning of yellowing and of *Ampelopsis hederacea* collected at the beginning of reddening were placed in bell jars with the base of each petiole in H_2O . Under these conditions the leaves continued to yellow or redden but more slowly than corresponding leaves on the branches. The app. contg. the leaves was placed in the open air near the plants from which the leaves were collected. Air deprived of CO_2 was pumped through the bell jars at the rate of 48 l. in 24 hrs. and afterwards passed through tubes contg. a soln. of $Ba(OH)_2$ when $BaCO_3$ was pptd. showing the presence of CO_2 . These $Ba(OH)_2$ tubes were replaced at the same hr. each day for 6 days and the amt. of CO_2 was detd. for each day. CO_2 evolved in mg. per g. of dry leaf during 24 hrs. ranged from 3.4 to 13.8, total 41.0 by *Fagus*; 4.2 to 7.2, total 33.1 by *Aesculus*; and 6.1 to 14.7, total 58.0 by *Ampelopsis*. The corresponding total amts. of carbohydrate for the 3 leaves were 27.8, 22.4, and 39.4 mg., resp., per g. of dry leaf.

L. W. RIGGS

Sand drown, a chlorosis of tobacco and other plants resulting from magnesium deficiency. W. W. GARNER, J. E. McMURTREY AND E. G. MOSS. *Science* 56, 341-2 (1922).—In this disease the veins and midrib of the tobacco leaf tend to retain their normal color but there is more or less complete blanching of the lamina, both yellow and green chlorophyll pigments being affected, thus differing from the chlorosis caused by K deficiency. The disease occurs in the more sandy portions of the field after a heavy rainfall. It is caused by an insufficient supply of Mg in the soil or fertilizer. The symptoms of Mg deficiency are intensified by increase in the amt. of SO_4 in the soil. The addition of $MgSO_4$ or $MgCl_2$ to the fertilizer prevents the disease. "Double manure salt" and "kainit" prevent the disease. The purer forms of K_2SO_4 result in a more severe chlorosis than that caused by KCl. Dolomitic limestone prevents the disease while pure calcite is ineffective. If not too far advanced, the disease is readily cured by the addition of Mg to the nutrient soln.

L. W. RIGGS

The phytosterols of ragweed pollen (Heyl) 10. The cultivation of tannin-producing acacias in French North Africa (Jalade)²⁹.

E—NUTRITION

PHILIP B. HAWK

NORMAL

The vitamins of yeast and their role in animal nutrition. CASIMIR FUNK AND H. E. DUBIN. *Proc. Soc. Exptl. Biol. Med.* 19, 15(1921).—One l. of autolyzed yeast was shaken with 50 g. of fuller's earth; the filtrate from this was inactive for avian heriberi, having lost vitamin B, but retained another euphoristic vitamin (D) which could be entirely removed by adsorbing twice with 100-g. portions of fuller's earth. Rats receiving the so-called synthetic diet with cod-liver oil as source of vitamin A, required both B and D vitamins for normal growth. When either was added separately, the animals ceased growing and died in a few months. C. V. B.

The antiscorbutic potency of strawberries. C. A. SMITH, OLAF BERGEHM AND P. B. HAWK. *Proc. Soc. Exptl. Biol. Med.* 19, 22(1921).—Several guinea pigs were fed a diet of oats, milk, and hay until they were decidedly scorbutic. The daily addn. to the diet of 10 cc. of strawberry juice caused the symptoms to disappear within 7 days. Juice previously boiled for 5 mins. had the same curative effect. Strawberries appear to be relatively rich in water-sol. C vitamin. C. V. B.

A globulin as the principal protein of the pecan nut: its chemical and nutritive properties. F. A. CAJORI. *Proc. Soc. Exptl. Biol. Med.* 19, 52(1921).—See C. A. 16, 577. C. V. B.

The destruction of antiscorbutic vitamin in milk by the catalytic action of minute amounts of copper. A. F. HESS AND L. J. UNGER. *Proc. Soc. Exptl. Biol. Med.* 19, 119(1921).—Diluted dry milk heated to 60° for 40 mins. in a Cu vessel was found to contain 1.4 parts of Cu per million. Guinea pigs fed on this milk in addn. to oats all developed scurvy and died after about 4 wks. Controls given the above diet + 2 cc., daily, of orange juice grew normally. Controls given similar portions of milk heated in a glass vessel and oats did not become scorbutic during a period of 4 mos. The minute trace of Cu may act as a catalyzer causing destruction of antiscorbutic vitamin. This factor should be considered in com. pasteurization or condensation of milk. C. V. B.

A delicate biological test for calcium-depositing substances. E. V. McCOLLUM, NINA SIMMONDS, P. G. SHIPLEY AND E. A. PARK. *Proc. Soc. Exptl. Biol. Med.* 19, 123(1921).—To young rats is given a diet which uniformly causes the epiphyseal cartilage and the metaphysis to be free from Ca salts, and at the same time permits growth and maintains a fair state of general health and nutrition. When losing control of the hind legs, the rats are divided into two groups and the substance to be tested is added to the diet of one group. When sufficient time has elapsed the animals are killed and the tibia is split lengthwise, one half being immersed in dil. AgNO₃ soln., exposed to light and examd. in the soln. through a binocular microscope. A newly formed line of calcification in the proliferative cartilage is sought. This line is blackened and looks like the cross section of a honeycomb under strong magnification. The food intake of test and control animals must be watched carefully as complete starvation causes the typical linear deposit of lime salts to appear. C. V. B.

Nitrogenous metabolism in exclusive feeding with seeds of *Lathyrus sativus*. DOMENICO LIOTTA. *Arch. farm. sper.* 34, 1-5, 17-23, 33-6(1922).—Two adult male albino rats were maintained in a healthy condition 6 and 7 weeks, resp., on an exclusive diet of meal prepd. from the seeds of *Lathyrus sativus*. A plus N balance and a slight gain in wt. were noted. A. W. DOX

Examination of unpolished rice. J. F. A. POOL. *Pharm. Weekblad* 59, 1079-82 (1922).—The P_2O_5 content of rice is a measure of the amt. of pericarp left on the grain and, therefore, an index of its ability to prevent beriberi. For the Dutch-Indian army a minimum of 0.37% P_2O_5 is required when rice forms a large component of the ration. In 61 samples of rice the P_2O_5 varied only slightly from 50% of the total ash. Since the detn. of total ash is more easily and quickly performed than that of P_2O_5 , it is recommended in place of the latter as a measure of ability to prevent beriberi. A. W. DOX

Yeast as a source of vitamin B for the growth of rats. CORNELIA KENNEDY AND L. S. PALMER. *J. Biol. Chem.* 54, 217-32 (1922).—Yeasts from different sources vary considerably in the amts. required to furnish adequate amts. of H_2O -sol. B to growing rats over periods of 2 to 4 months. These differences may be due to differences in species, character of medium in which grown or to the state in which the yeast is removed. Better results were obtained when the yeast was fed separately as a pellet than when it was mixed with the ration. Ten % yeast, with the addn. of 25 to 50 mg. N to the daily ration, is not so good a source of H_2O -sol. B as is 11.4% of EtOH ext. of wheat embryo, furnishing only 5 to 10 mg. N. The objections to the use of N compds. of unknown nature in expts. designed to study the relative value of certain proteins or amino acids are emphasized. Cf. following abstr. I. GREENWALD

The synthesis of water-soluble B by yeast grown in solutions of purified nutrients. MARGARET B. MACDONALD. *J. Biol. Chem.* 54, 243-8 (1922).—Each of 5 yeasts, including 1 pure culture each of *Saccharomyces cerevisiae* and *S. ellipsoideus*, grown in a mixt. of 1 l. H_2O , 50 g. sucrose, 2 g. KH_2PO_4 , 2.35 g. $(NH_4)_2SO_4$, 0.25 g. $CaCl_2$, and 0.25 g. $MgSO_4$ furnished adequate amts. of H_2O -sol. B when fed as 5% of the ration to growing rats over a period of 2 months. The basal diet consisted of 18.0% casein, 2.0% agar, 71.3% dextrin, 5.0% hutter fat and 3.7% of a mixt. of 0.173 g. $NaCl$, 0.266 g. $MgSO_4$, 0.347 g. $NaH_2PO_4 \cdot H_2O$, 0.954 g. K_2HPO_4 , 0.540 g. $CaH_4(PO_3)_2 \cdot H_2O$, 0.118 g. Fe citrate and 1.300 g. Ca lactate. Cf. C. A. 15, 2465 and preceding abstr. I. G.

Studies in inorganic metabolism. I. Interrelations between calcium and magnesium metabolism. L. JEAN BOGERT AND ELIZABETH J. MCKITTRICK. *J. Biol. Chem.* 54, 363-74 (1922).—Four young women were fed a const. analyzed diet which furnished 2 of them 2000 cal., 62 g. protein, 48 g. fat, 0.266 g. Ca and 0.275 g. Mg and the other 2, 2208 cal., 66 g. protein, 57 g. fat, 0.309 g. Ca and 0.292 g. Mg. All maintained their wt. throughout the exptl. period, which was divided into 4 periods of 4 days each. In the second period, 6 g. Mg citrate (0.771 g. Mg) and in the fourth period, 6 g. Ca lactate (0.769 g. Ca) were added to the daily diet. The addition of Mg citrate increased the excretion of Mg in both urine and feces and of Ca in the feces in all 4 subjects and of Ca in the urine of 3. The addition of Ca lactate increased the excretion of Ca in urine and feces in all 4 subjects. The effect on Mg excretion was not absolutely clear but, apparently, this was also slightly increased. II. The effects of acid-forming and base-forming diets upon calcium metabolism. L. JEAN BOGERT AND ELIZABETH E. KIRKPATRICK. *Ibid* 375-86.—Two normal women received in the first and third periods of 4 days each, analyzed diets furnishing 2222 cal., 68 g. protein, 61 g. fat, 0.297 g. Ca and an excess of acid-forming elements equiv. to 2 cc. N acid. In the second and fourth periods, the energy, protein and fat content of the diet remained practically unchanged but in the former the food contained 0.260 g. Ca and an excess equiv. to 55 cc. N alkali and, in the latter, 0.319 g. Ca and an excess equiv. to 60 cc. N acid. In two other women, the basal diet furnished 1968 cal., 64 g. protein, 48 g. fat, 0.242 g. Ca and an excess of 2 cc. N acid, changing to 0.223 g. Ca and an excess of 45 cc. N alkali in the second period and to 0.287 g. Ca and an excess of 54 cc. N acid in the fourth. The subjects maintained their wt. In 2 subjects, the acid-forming diet led to an increased negative Ca balance, in a third the total Ca excretion was increased but not the

negative balance and, in the fourth, the result was obscured by digestive disturbances. The total Ca excretion was diminished in the period of base-forming diet in 3 subjects and was almost unchanged in the fourth. In 2 instances the negative balance was diminished, in 2 others it was increased. The base-forming diet increased the fecal Ca and lowered the urinary Ca, whereas the acid-forming diet had the opposite action.

III. The influence of yeast and butter fat upon calcium assimilation. L. JEAN BOGERT AND RUTH K. TRAIL. *Ibid* 387-97.—The ingestion of 84 g. commercial compressed yeast to daily diets furnishing 0.341 and 0.395 g. Ca daily led to a lowered excretion in 3 of 4 women and to no demonstrable change in the other. The substitution of an equal wt. (50 g. in 2 expts., 72 g. in 2 others) of butter fat for the nut margarine in the basal diet resulted in a lowering of the negative Ca balance in 2 cases, in Ca equil. in another and in a positive balance in the fourth. (All had been in negative Ca balance.)

I. GREENWALD

The growth-promoting factor of lemon juice. I. How is the growth-promoting factor for bacteria influenced by physical, chemical and colloid-chemical processes. B. LEICHTENTRITT AND M. ZIELASKOWSKI. *Biochem. Z.* 131, 499-512(1922).—Studies of the growth-promoting effect of lemon juice on diphtheria bacilli. The growth-promoting factor is largely dialyzable. Heating of the lemon juice to 100° and in the autoclave rather tends to enhance its activity than otherwise and the reaction whether acid or alk. seems to play no important role. Hydrolysis with 2 to 3% HCl does not destroy the effective factor, while hydrolysis with NaOH does so. Radiation of the lemon juice with ultra-violet light or X-rays is without effect, even if heat is simultaneously employed. Furthermore, aeration of the heated juice does no harm. If lemons are allowed to stand at room temp. they do not show a decrease in their growth-promoting properties. On the other hand when the juice is shaken with kaolin, charcoal or talc there is a decrease, but not to completeness, in the growth-promoting factor, and this effect is not altered by previous treatment. The property of dialysis is independent of the acid reaction of the juice.

F. S. HAMMETT

The growth-promoting factor of lemon juice. II. Comparative studies with guinea pigs and bacteria. B. LEICHTENTRITT AND M. ZIELASKOWSKI. *Biochem. Z.* 131, 513-24(1922).—Guinea pigs are protected from scurvy for a long time but eventually become sick when fed lemon juice which has been heated twice for 1-hr. periods in the autoclave. The action of ultra-violet light and aeration, with and without heat, on lemon juice does not destroy its antiscorbutic properties. Adsorption by kaolin, talc, etc., and dialysis of the juice remove its antiscorbutic properties, as does aging. All of these processes fail to inhibit the growth-promoting effect on bacteria, although adsorption and dialysis weaken the availability. Hence, it is concluded that lemon juice possesses the antiscorbutic factor C; and a growth-promoting factor, which is effective in under-sized children and bacteria. It is the vitamin D of Funk.

F. S. HAMMETT

Can the disturbances of growth induced by lack of vitamins be influenced by chemically defined substances? D. OGATA. *Biochem. Z.* 132, 89-94(1922).—Six groups of rats of only 3 in each group were fed as follows: Group A, normal diet plus butter; group B, diet of group A plus NaI; group C, diet of group A plus thyroid substance; group D, vitamin-free diet of polished rice plus salt mixt.; group E, diet of group D plus NaI; group F, diet of group D plus thyroid substance. 0.025 g. of NaI was given for 3 rats and 0.01 g. thyroid prepn. on the basis of that amt. per 100 g. of rat wt. Notwithstanding the very small number of rats used in each group and the known variability of increments of wt. of the rat, as compared with group A, all other groups were retarded in growth by the diets used.

F. S. HAMMETT

The metabolism of pigeons deprived of vitamin B. F. CARIDROIT. *J. physiol. pathol. gen.* 20, 189-92(1922).—When pigeons are fed on polished rice the respiratory

metabolism remains fairly const. for the 1st week and then drops greatly. The respiratory quotient, which at first is 0.9 in both controls and tests, falls to 0.7 and then is increased to 0.8 at the moment of seizures. There is a marked decrease in N elimination. The injection of histamine does not modify the respiratory coeff. F. S. HAMMETT

The present status of our knowledge of vitamins with particular reference to their clinical significance. WILHELM STREPP. *Klin. Wochschr.* 1, 881-5, 931-5(1922).—

MILTON HANKE

Further experiments on the isolation of the antineuritic vitamin. ATHERTON SEIDELL. *J. Am. Chem. Soc.* 44, 2042-51(1922); cf. *C. A.* 16, 578.—Highly active vitamin fractions can be isolated from yeast by adding the fresh yeast to boiling H_2O , heating a few min., boiling or centrifuging, prepg. from the resulting clear soln. (which contains a greater proportion of the total vitamin than the soln. obtained by the autolysis method and is free from adenine and other products of autolytic decompn.) a fuller's earth adsorption compd. (the so-called "activated solid"), extg. with $Ba(OH)_2$, removing the Ba with H_2SO_4 , pptg. with $Pb(OAc)_2$, removing the excess of Pb with H.S, concg. *in vacuo* and pptg. successively with $AgNO_3$ and NH_4AgNO_3 . Approx. $1/5$ of the solids of the ext. is pptd. as Ag compds. and these contain somewhat more than 0.5 of the antineuritic vitamin; the incomplete pptn. of the vitamin base is believed to be due to the considerable soly. of its Ag compd. The vitamin fractions so obtained are quite stable both in soln. and when dry. They dialyze almost completely through celloidion, all of the vitamin being found in the diffusate, thus indicating that its mol. is relatively simple. With N detns. as a criterion of purity, it is concluded that the highly active fractions contain vitamin and one or more analogous N bases and that these cannot be advantageously sepd. by Ag pptn. C. A. R.

Present state of our knowledge of the vitamins and its application to the dietary. H. C. SHERMAN, C. E. A. WINSLOW, E. J. FISK, I. GREENWALD AND T. P. B. JONES. *Am. J. Pub. Health* 12, 908-15(1922).—A resumé. NATHAN VAN PATTEN

Studies on vitamins B and D. CASIMIR FUNK AND JULIA B. PATON. *J. Metabolic Research* 1, 737-75(1922).—Pigeons are claimed to be more suitable for testing vitamin B than rats, because of complicated vitamin requirements of the latter. A shorter procedure of testing B on pigeons is described, employing single pigeons in each cage, rather than groups of birds. Further evidence is presented on the vitamin-sparing action of certain proteins known to be free of vitamin B (cf. *C. A.* 15, 550). Increased carbohydrate feeding did not give clear results as regards an increased vitamin requirement. Increasing the amt. of vitamin B did not increase the intake of a well balanced diet. Individual pigeons show great variations in their requirement of vitamin B which is of great importance in interpreting results of vitamin test on these birds. Slight evidence is adduced that with diminished food intake beriberi symptoms are delayed on a diet free from vitamin B. Alkali and also autoclaving at 25 lbs. for 3 hrs. destroy vitamin B and have a much smaller effect on vitamin D. Growth of yeast or of some other fungus removes vitamin D out of soln. and leaves B in soln. This method can be used for the elimination of vitamin D from a mixt. of B and D. The yeast cells retain vitamin D very tenaciously after they have taken it out of soln. W. A. P.

The variety of minimal substances in the nutrition of children. HENRI GODLEWSKI. *Presse med.* 30, 256-7(1922).—A review of the role of vitamins and of their distribution in various foods. W. A. PERLZWEIG

Remarks on "The role of the vitamins in the chemistry of the cell" by W. R. Hess. E. ADERHOLDEN. *Z. physiol. Chem.* 122, 88-92(1922). R. L. STEHLE

Vitamins. I. Gas metabolism of white mice on a vitamin-free diet. FRANZ GROEBBELS. *Z. physiol. Chem.* 122, 104-24(1922).—The O consumption and wt. curves parallel each other. R. L. STEHLE

ABNORMAL

The prevention of the development of rickets in rats by sunlight. P. G. SHIPLEY, E. A. PARK, G. F. POWERS, E. V. MCCOLLUM AND NINA SIMMONDS. *Proc. Soc. Exptl. Biol. Med.* 19, 43-7(1921).—Eighteen young rats were placed on a diet which contains nearly twice the optimal content of Ca, is well constituted, but decidedly low in P and fat-sol. vitamin. This diet produces rickets comparable to that of human beings. Six of the rats were kept under usual lab. conditions in a well ventilated room having windows of ordinary glass; when killed at the end of 2 mos., all showed gross and microscopic signs of rickets. The remaining 12 rats were daily exposed to direct sunlight, spending, on an av., 4 hrs. out of doors during the 62-67 days of observation. Rickets did not develop in these animals. Sunlight, like the action of cod-liver oil, raises the potential of cellular activity with a resulting max. utilization of the substances available in the body, which are concerned with ossification and calcification. C. V. B.

Experimental rickets. J. R. MCCLENDON AND HARRY BAUGUESS. *Proc. Soc. Exptl. Biol. Med.* 19, 59-61(1921).—A diet consisting largely of white wheat flour caused no lasting bone abnormalities in albino rats. Casein as a substitute for lactalbumin or edestin caused bone changes in all cases. If casein constituted but 6% of the ration, the abnormalities were reduced but persisted despite the hardening of the bones and their casting dense X-ray shadows. The deformities did not disappear when the diet was changed to wheat flour with 6% sea salt, or on the addn. of lactalbumin, edestin, or sources of vitamins A and B. The X-rays and Ca balance indicate the severity of the disorder. C. V. B.

The basal metabolism in nontoxic goiter and in horderline thyroid cases, with particular reference to its bearing in differential diagnosis. J. H. MEANS AND HARRIET W. BURGESS. *Arch. Intern. Med.* 30, 507-16(1922).—Patients who do not have an outspoken clinical picture of hyperthyroidism or of hypothyroidism, but in whom the thyroid is probably involved do not, in most cases, show an abnormal basal metabolism. However, an abnormal basal metabolism, in the absence of other well recognized causes, is presumptive evidence of disordered thyroid function. I. GREENWALD

Experimental rickets in rats. IX. The distribution of phosphorus and calcium between the skeleton and soft parts of rats on rachitic and non-rachitic diets. GERTRUDE F. MCCANN AND MARION BARNETT. *J. Biol. Chem.* 54, 230-12(1922).—In rats, in which rickets had been induced by the feeding of diets poor in Ca and rich in P, or rich in Ca and poor in P, the content of P and Ca per 100 g. of body wt. was less than in normal rats. The deficiency was greatest in those animals that had grown most, and, in these rats the P of the bone constituted a smaller fraction of the total P of the body than in normal rats. The ratio Ca:P in the bones was not changed from the normal. "When rickets is prevented from developing in rats given a diet poor in P but rich in Ca by administration of cod-liver oil or by exposure to light, the total P and Ca content per 100 g. body wt. is well within the normal range." I. GREENWALD

Studies on experimental rickets. XXIII. The production of rickets in the rat by diets consisting essentially of purified food substances. E. V. MCCOLLUM, NINA SIMMONDS, J. ERNESTINE BECKER AND P. G. SHIPLEY. *J. Biol. Chem.* 54, 249-52(1922).—Rickets developed in rats kept on a diet of (A) wheat germ, extd. with Et_2O and CHCl_3 , 3%, purified wheat gluten 15%, gelatin 15%, agar 2%, salt mixt. 3.9%, CaCO_3 1.5%, purified dextrin 56.96%, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ 0.64%, butter fat 2% or (B) extd. wheat germ 3%, wheat gluten 5%, gelatin 5%, casein 5%, agar 2%, salt mixt. 3.9%, CaCO_3 1.5%, dextrin 72.6%, butter fat 2%. The salt mixt. contained 1.5 g. CaCO_3 , 1.0 g. KCl , 0.5 g. NaCl , 0.7 g. NaHCO_3 and 0.2 g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. (A) contained 0.533 g. K, 0.517 g. Na, 1.202 g. Ca, 0.010 g. Mg, 0.173 g. S, 0.781 g. Cl and 0.217 g. P per 100 g. (B) contained 0.533 g. K, 0.411 g. Na, 1.202 g. Ca, 0.010 g. Mg, 0.121 g. S, 0.781 g. Cl and 0.088

g. P. Xerophthalmia developed in both series, in spite of the presence of fat-sol. A in the diet. Cf. C. A. 16, 3686. I. GREENWALD

Antiketogenesis. IV. The ketogenic-antiketogenic balance in man and its significance in diabetes. P. A. SHAFER. *J. Biol. Chem.* 54, 399-41 (1922); cf. C. A. 15, 3307.—*In vitro* expts. with excess of acetoacetic acid indicate that 1 mol. of glucose will accelerate the oxidation of 2 mols. of acetoacetic acid with H_2O_2 . But calcs. made upon this basis, with the previously accepted ketogenic and glycogenic equivalents of fat and protein, from the data obtained with severe diabetes, do not yield values for acetone bodies as high as those actually observed. S. believes the old value for the ketogenic equiv. of protein is too high and now employs the factor 15 with which to multiply the number of g. of N in the urine in order to obtain the number of millimoles of acetoacetic acid derived from the metabolized protein. The data obtained by S. and by others upon patients with severe diabetes or upon normal persons on high-fat, low-carbohydrate diets are analyzed to show their substantial agreement with this hypothesis. In mild ketosis, the ratio of ketogenic to antiketogenic equivalents may be anywhere between 1 and 2. The minimum amt. of glucose required to obtain ketogenic equil. is calcd. as $\{ \text{total cal. of metabolism} - (\text{urine N} \times 130) \} \div 50$. This is the theoretical minimum and should generally be doubled in order to allow for the variations in the character of the metabolism during the day. I. GREENWALD

Studies on qualitative undernourishment. I. The beriberi of rats. FRANZ HOFMEISTER. *Klin. Wochschr.* 1, 522-3 (1922).—Rats fed on a diet deficient in vitamin B show all of the symptoms that are characteristic of a central nervous system derangement. Such animals show multiple hemorrhages in the cerebellum and in the brain stem, together with nervous degeneration in these parts. The peripheral nerves were, in many cases, not at all degenerated. The same anatomical changes occur in pigeons that have been fed exclusively on polished rice. In these cases the term hemorrhagic encephalitis is more appropriate than polyneuritis. In man and in the chicken the peripheral nerves seem to be attacked first. MILTON HANKE

Metabolism studies in tetany. F. P. UNDERHILL, WILDER TILESTONE AND L. JEAN BOGERT. *J. Metabolic Research* 1, 723-30 (1922).—On a Ca-rich diet (milk) patients with tetany tend to store temporarily a larger than normal amt. of Ca. On the other hand on a Ca-poor diet the stored Ca is eliminated to a much greater extent than occurs in the normal subject. In tetany, relatively little Ca is eliminated in the urine, and while relatively large amts. are excreted in the stools, this represents in large measure excretion of absorbed Ca rather than the direct passage through the alimentary canal of ingested Ca. The Ca content of the blood was found to be distinctly lower than in normal subjects, the low level of the blood Ca being quite independent of the relative amts. of Ca ingested. In tetany a patient may steadily lose wt. and yet maintain a positive N balance and exhibit a normal N utilization. The most characteristic feature of the urinary excretion is the large output of NH_4 , the elimination of which does not appear to be directly associated with any other urinary evidences of acidosis (pH , org. acidity, total acidity and P). Fat utilization in the patient studied was very poor. It is probable that this aspect is associated with the accompanying severe diarrhea and the marked loss of body wt. On the basis of the tendency to store Ca in tetany as possibly representing a Ca need it is suggested that Ca administration may be desirable in this condition. W. A. PERLZWEIG

Advanced chronic nutritional disturbances in infancy. KIRSTEN UTHEIM. *J. Metabolic Research* 1, 803-917 (1922).—An extensive study of etiology, symptomatology and pathogenesis of nutritional disturbances in infants, for which U. suggests the generic term *athrepsia*. A study of the chem. compn. of the blood and urine under varying clinical conditions is included. A review of the literature and a large bibliography are given. W. A. PERLZWEIG

F—PHYSIOLOGY

ANDREW HUNTER

A comparison of the waves of blood pressure produced by slow and by rapid breathing. ROBERT TROTTER, PHILIP EDSON AND ROBERT GESELL. *Proc. Soc. Exptl. Biol. Med.* 19, 57(1921).—A *cardio-respiratory wave* of systolic blood pressure is one produced during a single normal respiratory cycle; the highest pressure is at the beginning of inspiration. *Cardio-respiratory interference waves* are elicited by rapid breathing, the wave being produced during a series of respiratory cycles. The highest pressure is approx. at the beginning of expiration. These waves occur when the no. of respirations are 1 less or 1 greater than the no. of heart beats in a wave time-interval. If the respiratory rate is slightly slower or slightly faster than half the heart rate, *double interference waves* are produced, being formed, resp., by the odd and even numbered heart beats. The work explains some cases of pulsus alternans and blood pressure waves of the third order. C. V. B.

The physiology of the gall bladder. L. S. AUSTER AND B. B. CROHN. *Proc. Soc. Exptl. Biol. Med.* 19, 117(1921).—Laparotomy and duodenotomy were done on 8 chlorotomized dogs. All but one showed distended gall bladders. Methylene blue was injected into the bladder to color its contents. Slight digital pressure sufficed to expel the contents. Irrigation of the duodenal mucosa, including the papilla of Vater, with solns. of $MgSO_4$, Na_2SO_4 , Na phosphate, peptone, 0.1 N HCl, bile, or Na glycerophosphate caused an increased flow of bile from the liver, but no expulsion of the gall bladder contents. Strong direct faradic stimulation failed to produce contraction or expulsion. Refilling of forcibly emptied gall bladders was a slow and irregular process. Stasis of contents was detd. by injecting charcoal or carmine into the bladder; after periods up to 3 days of regular mixed diet, autopsies revealed the presence of the pigment in the bladder contents; expulsion was complete in 1 week. Phenoltetrachlorophthalein, injected intravenously, reappeared in the bile in 10–15 min.; it was found in the gall bladder contents when the cystic duct was patent, but was not present when the duct had been tied off. C. V. B.

Relation of splenectomy to growth and appetite in the rat. A. H. SMITH AND J. E. ASCHAM. *Proc. Soc. Exptl. Biol. Med.* 19, 127(1921).—Sixteen 40-day old rats were splenectomized and fed according to the standard technic of Osborne and Mendel. Observation from 34 to 43 weeks failed to detect any increase of appetite or variation from the normal growth rate. Eight of these were the progeny of splenectomized rats, and of the 5 examd. none showed an abnormal erythrocyte count. C. V. B.

The toxicity of asphyxiated blood. RINALDO PELLEGRINI. *Arch. farm. sper.* 24, 60–4, 70–80(1922).—The transfusion of hirudinated normal blood obtained from healthy animals causes disturbances varying in intensity with the dose. The most serious of these are dyspnea, somnolence, immobility, thirst, paresis, sometimes exophthalmus and uridriasis. The temp. may fall as low as 33°. With transfusion of 60–80 cc. per kg. the recipient animal dies within 2 days with convulsions, midriasis and exophthalmus. Hirudinated asphyxiated blood causes the same disturbances but the sensitivity of the recipient is more variable. Large doses are less harmful than corresponding doses of normal blood. Transfusion of serum, whether normal or asphyxiated, is better tolerated than that of blood. Normal serum in large doses (65 cc. per kg.) is not fatal, while 20–40 cc. per kg. of asphyxiated serum is sometimes fatal and 40–50 cc. sometimes entirely without effect. There is no evidence in support of the supposed toxicity of asphyxiated blood. A. W. DOX

Evaluation of buffers of the blood. E. A. DOISY, A. P. BRIGGS, E. P. EATON AND WM. H. CHAMBERS. *J. Biol. Chem.* 54, 305–29(1922); cf. following abstr.—Of the

total CO_2 carried in the blood in the change from the arterial to the venous state, about 53% is carried isobrydically (without change of p_H) in the change from oxyhemoglobin to reduced hemoglobin; about 27% is due to the change in the reaction within the corpuscles and about 12% is due to CO_2 physically dissolved. Less than 5% is due to the buffer action of the sepd. serum and less than 1% to the inorg. P of the cells. The values for CO_2 content obtained with fully oxygenated blood are corrected for O_2 unsatn. by adding the product of the % unsatn. by the factor (experimentally detd.) 0.27.

I. GREENWALD

Studies of gas and electrolyte equilibrium in the blood. III. The alkali-binding and buffer values of oxyhemoglobin and reduced hemoglobin. D. D. VAN SLYKE, A. B. HASTINGS, MICHAEL HEIDELBERGER AND J. M. NEILL. *J. Biol. Chem.* 54, 481-506(1922); cf. C. A. 16, 3918 and preceding abstr.—The alkali (Na) bound at $p_H = 7.4$ per g. mol. of recrystd. horse oxyhemoglobin (HbO_2) (amt. combining with g. mol. of O_2) has been detd. to be 2.15 ± 0.10 equivs., that per g. mol. of reduced hemoglobin (Hb) to be 1.47 ± 0.08 . The errors indicated are about half due to the combined analytical errors and about half to the presence of 7 to 20% of Hb, in the preps. used, in a form incapable of binding labile O_2 . At $p_H 7.4$, the change from Hb to HbO_2 enables the g. mol. to combine with 0.68 ± 0.10 equivs. of additional alkali. For points intermediate between complete oxygenation and complete reduction, the increase in base bound at const. p_H is directly proportional to the increase in O_2 content. The mol. buffer values (increase in base bound for each change of 0.1 in p_H) are 2.64 for HbO_2 and 2.45 for Hb, over the range $p_H 7.2$ to 7.5 and very nearly these figures from $p_H 7.0$ to 7.6. The relations may be expressed by the equation $B = 2.64 (\text{HbO}_2) (p_H - 6.583) + 2.45 (\text{Hb}) (p_H - 6.80)$. The values of 2.64 and 2.45 for the mol. buffer values indicate that at $p_H 7.2$ to 7.5 at least 5 monovalent acid groups share in the alkali combined with the Hb. IV. The effect of oxygenation and reduction on the bicarbonate content and buffer value of blood. D. D. VAN SLYKE, A. B. HASTINGS AND J. M. NEILL. *Ibid* 507-26.—The av. buffer value at $p_H 7.2$ to 7.5 of 3 samples of oxygenated blood from the same horse was found to be 25.3 millimols. the av. for reduced blood 24.4 millimols. The difference is attributed to the fact that the loss in buffer action when HbO_2 is reduced is only partly compensated for by the accompanying increase in BHCO_3 . Any single specimen of blood, the degree of oxygenation being const., gave const. values over the range $p_H 7.2$ to 7.5. In oxygenated blood, HbO_2 was calcd. to be responsible for 76.0% of the buffer value and BHCO_3 for 6.9%; in reduced blood, Hb for 73.3% and BHCO_3 for 9.0%. At $p_H 7.3$, the decrease in BHCO_3 per added mol. of O_2 combined with Hb in the blood varied between 0.50 and 0.59. The variation is outside the limit of error and appears to be due to variable factors of unknown nature. The ratio in blood is lower than in Hb solns. (cf. preceding abstr.). Between the limits $p_H 7.2$ and $p_H 7.5$, the ratio of decrease in BHCO_3 to increase of O_2 combined with Hb is increased by about 0.02 for each rise of 0.1 in p_H . No quant. differences were observed between defibrinated blood and blood in which coagulation had been prevented by the addn. of 0.2% $\text{K}_2\text{C}_2\text{O}_4$ and 0.1% NaF.

I. GREENWALD

The excretion of acid and ammonia. R. S. HUBBARD AND S. A. MUNFORD. *J. Biol. Chem.* 54, 465-79(1922).—Twenty-one expts. were carried out on 19 subjects who did not show clinical or metabolic symptoms of acidosis. Six of these had gastric anacidity. Specimens of urine were collected every 2 hrs. during the day and then a single 12 hr. specimen was obtained. The urines from the patients with anacidity showed a high degree of constancy of H^+ and NH_3 concn. throughout the day. All the data obtained were submitted to statistical analysis, from which it is concluded there was a direct relation between the vol. of urine and the amt. of NH_3 excreted and between the concn. of NH_3 and the acidity (H^+ concn.) of the urine. All other rela-

tions observed appeared to be secondary to these. The observations are interpreted to support the view that NH_3 is formed in the kidney. Cf. Nash and Benedict, *C. A.* 16, 117.

I. GREENWALD

The influence of the relative moisture of the air on insensible water excretion of the skin. O. MOOG. *Deut. Arch. klin. Med.* 138, 181-92(1922).—With 5 people it was shown that by variations in the moisture of the air of 30-40% and with an av. temp. of 25° the excretion of H_2O through the skin is more in higher humidities than in lower ones. This indicates that H_2O secretion by the skin is a physiol. process that assists in heat regulation.

JULIAN H. LEWIS

Influence of glands with internal secretions upon the respiratory exchange. V. Further observations on the effect of suprarenal insufficiency (by removal) in thyroidectomized rabbits. DAVID MARINE AND EMIL J. BAUMANN. *J. Metabolic Research* 1, 777-802(1922); cf. *C. A.* 15, 1752, 3519; 16, 2719.—Thyroidectomy abolishes or greatly lessens the rise in heat production which normally follows sufficient injury of suprarenal function in rabbits. Additional evidence is furnished of the existence of a thyroid-suprarenal cortex interrelationship, which is sep. from the thyroid-chromophil tissue interrelationship. The nature of this relationship is unknown, but the evidence suggests that the suprarenal cortex exercises an inhibitory or regulatory control over thyroid activity; and when this is sufficiently injured the thyroid automatically responds with increased functional activity, resulting in increased heat production if a sufficient amt. of I-contg. hormone is liberated. Evidence is also shown that single doses of I (25 mg. KI) administered by mouth increase the heat production in suprarenal-ectomized rabbits with incomplete thyroidectomy; and that sufficient but sub-lethal suprarenal insufficiency in rabbits and in cats causes a rapid loss of I from the thyroid. W. A. P.

The role of diffusion in the absorption of gases and in the maintenance of sub-atmospheric pressure in the pleura. E. RIST AND A. STROEL. *Presse med.* 30, 69-71 (1922).—An application of the law of partial pressure of gases to conditions existing in the pneumothorax, expressed in terms of the equil. existing between the tension of the gases in the chest cavity and the tension of the gases in the body fluids. W. A. P.

The metabolism of fats. H. ROGER AND LEON BINET. *Presse med.* 30, 277-9 (1922).—The authors analyzed the total fat content of dog blood before and after its passage through the lungs, also after permitting arterial and venous blood and various organs and tissues to autolyze at 38° for 18 hrs. They found a considerable loss of fat in the blood during its passage through the lungs, also a greater destruction of fat in autolyzing lung tissue than in any other tissue with the exception of the liver. They suggest that the lungs play a role in the catabolism of fats analogous to that of the liver in the catabolism of proteins and carbohydrates.

W. A. PERLZWEIG

Anticoagulants. J. P. LANGLOIS AND LEON BINET. *Presse med.* 30, 501-2(1922).—A review of anticoagulating agents used with blood, including nucleoprotein derivs., Na citrate and arsenobenzenes. Some expts. are cited showing the effect of temporary retardation exercised by arsenobenzenes upon coagulation, and their use in blood transfusions is suggested.

W. A. PERLZWEIG

The causes of emigration of leucocytes. K. J. FERINGA. *Proc. Acad. Sci. Amsterdam emigration* 25, 36-41(1922).—Upon injecting widely varying org. and inorg. substances into the abdominal cavity of animals F. observed an invariably resulting exudation with emigration of many leucocytes, the result being entirely independent of the nature of the injected substance. From this he concluded that the emigration is not brought on by a sp. chemotactic influence of the definite substances upon the leucocytes. It was simultaneously observed that soon after the injections the p_H of the abdominal exudate invariably changed from the normal of 7.6 to 7.2, without any relation to the initial reaction of the injected fluid. When this development of acidity was temporarily checked by

injecting sufficiently large quantities of alkali the migration of leucocytes into the cavity was entirely inhibited. From this it is inferred that emigration of leucocytes is caused by the potential difference between the blood and the more acid fluids in inflammatory abscesses, the process being of the nature of cataphoretic action. In other abnormal accumulations of leucocytes in the body, as in leucemia, corresponding factors may play a part.

W. A. PERLZWEIG

The environment of the germ plasm. IX. Lowering of the body temperature of young Norway rats (*Mus decumanus*) by chemical agents and its influence upon tail length. J. A. BIRRENS DE HAAN AND H. PRZIBRAM. *Arch. Entwickl. Organ.* 50, 13-40 (1922).—Albino rats 3-4 weeks old acquire in the next 9-11 days a relative shortening of the tail if their body temp. is lowered by injection of fever-reducing agents. This effect is more noticeable the smaller the growth injury produced by the poisonous secondary effect and holds for both antipyrine and quinine. The effect on tail length is not traceable to growth restriction resulting from unfavorable conditions. In un-injected control animals, tail shortening is greater at lower than at higher external temps. The continuous shortening of relative tail length brought about by a lowering of external temp. is traceable to the simultaneous lowering of internal body temp. and not to the stimulating effect of external temp. Fasting expts. show that increase in tail length due to increased external temp. cannot be ascribed to insufficient food intake but to increased body temp. due to increased external temp.

CHAS. H. RICHARDSON

Decomposition of carbohydrates in striated muscle. II. FRITZ LAQUER. *Z. physiol. Chem.* 122, 26-45(1922); cf. *C. A.* 16, 2545.—In contrast to the months of February, March and April it is not possible in November, December and January to lower the glycogen content of frog muscles by maintaining the animals for 8 days at 25-27°. Neither does similar treatment enable such muscle to convert dextrose into lactic acid; glycogen is converted, but to a smaller extent than in spring and summer frogs. In concns. of 5-10% as well as in 2% solns. glycogen is a better lactic acid former than dextrose. Destroying the cell structure by freezing with liquid air prevented the conversion of dextrose to lactic acid by the muscle of summer frogs, but did not affect the conversion of glycogen. This is interpreted to mean that normally dextrose must first be changed into some other form before it is utilizable by muscle (a form directly derivable from glycogen) and that this change depends upon an intact cell structure.

R. L. STEHLÉ

Furylalanine. L. FLATOW. *Z. physiol. Chem.* 122, 143-4(1922).—A correction. Cf. *C. A.* 5, 1459. The analytical results are for the benzoyl deriv., not for furylalanine itself.

R. L. STEHLÉ

The present status of the function of the thyroid gland. DAVID MARINE. *Physiol. Rev.* 2, 521-51(1922).—A concise review including consideration of the chemistry of the thyroid. No new material. Extensive bibliography.

H. G. WELLS

The physiology of creatine and creatinine. ANDREW HUNTER. *Physiol. Rev.* 2, 586-626(1922).—An extended critical review with full bibliography. No new material.

H. G. WELLS

Blood destruction during exercise. I. Blood changes occurring in the course of a single day of exercise. G. O. BROWN. *J. exper. Med.* 36, 481-500(1922).—There is an increase in the % of cells and hemoglobin in the blood of the jugular vein which occurs early in the course of exercise. It probably results from a redistribution of red corpuscles, with an increase in their proportion in the peripheral blood. As exercise is continued, there is a definite increase in plasma vol. A coincident decrease in the total cell vol. and the pigment vol. during prolonged exercise suggests that blood destruction then occurs.

C. J. WEST

Oxygen content of cutaneous blood (so-called capillary blood). CHRISTEN LUNDS-

GAARO AND EGGERT MÖLLER. *J. exper. Med.* 36, 559-73(1922).—A method is given whereby cutaneous blood from a finger tip can be obtained for gas analysis without coming in contact with the air. The arterial and cutaneous blood from a normal resting individual showed about the same O content (97.5 and 96.6% of the total O-combining power of the blood). Venous blood drawn simultaneously was 75% satd. It is thought that this identity of arterial and cutaneous blood may be extended to the content of sugar, salt, uric acid, etc., and also to the reaction of the blood. Unless the perfusion of the skin has been extremely great during the expt. samples of blood from an incision in the skin (of the finger) cannot represent the true capillary blood. C. J. WEST

G—PATHOLOGY

H. GIDEON WELLS

The toxicity of placenta lipoids and their significance in the etiology of puerperal eclampsia. H. SCHÖNFELD. *Deut. med. Wochschr.* 47, 270-1(1921).—Dried and powd. placenta was extd. with either alc., ether, acetone, or petroleum ether. The exts. were evapd. *in vacuo*, suspended in saline, and tested on mice. Among the placenta lipoids are substances with physiol. activity (producing hyperemia, stimulating growth of the sexual organs, inducing labor) and substances with pronounced toxicity producing tissue lesions (convulsions, degeneration in parenchymatous organs, lesions of endothelium with thrombi and edema). The results are to be published more fully elsewhere.

S. AMBERG

The yellow discoloration (xanthochromia) of cerebrospinal fluid. E. LIESCHKE. *Deut. med. Wochschr.* 47, 376-7(1921).—Xanthochromia of the cerebrospinal fluid is due to the formation of bilirubin from hemoglobin. This could be shown by the indirect diazo reaction for bilirubin of Heijmans van den Bergh which permits the demonstration of bilirubin in 1:1 $\frac{1}{2}$ million concn. Xanthochrome fluid absorbs O_2 as does bilirubin. Washed red blood corpuscles introduced in the spinal canal produce in the course of a few days a yellow color of the cerebrospinal fluid and the fluid gives the bilirubin reaction. The production of bilirubin from red blood corpuscles in the test-tube was not successful. The production of bilirubin is laid to the action of an enzyme furnished by the endothelial cells.

S. AMBERG

Precipitin reaction in the dark field and in the hanging drop and its forensic applicability. G. STRASSMANN. *Deut. med. Wochschr.* 47, 556-7(1921).—Marx recommended a method of carrying out the precipitin reaction with very small amts. of suspicious blood exts. and antiserum for forensic purposes with the utilization of the dark field microscope. The method was found useful, but not more than the capillary method of Hauser.

S. AMBERG

A combined Sachs-Georgi-Wassermann reaction. A. STUEHMER AND K. MERZ-WEILER. *Deut. med. Wochschr.* 47, 559(1921).—The flocculent ppt. of a Sachs-Georgi reaction was centrifuged and washed. After taking up the flocs in saline, the complement and hemolytic system was added. There was an abundant sepn. of flocculent ppt. together with a complete inhibition of hemolysis.

S. AMBERG

Experimental investigations concerning the caseosan activity. K. BEHNE. *Deut. med. Wochschr.* 47, 583-5(1921).—By means of the complement-fixation method it was shown that serum of men and women contain antibodies for cows as well as human casein.

S. AMBERG

Artificial virulence and chemistry. H. MUCH. *Deut. med. Wochschr.* 47, 621-2 (1921).—Several bacteria which were not virulent when injected into animals became virulent when an acid such as lactic acid was injected with the bacteria intraperitoneally. Acid alone was not toxic in the amts. given. The acid may be neutralized. Addn. of

amts. as small as 0.001% lactic acid to broth cultures of hay bacilli rendered these bacilli virulent for mice. S. AMBERG

New investigations on the permeability of red blood corpuscles. E. WIECHMANN. *Deut. med. Wochschr.* 47, 824-5(1921).—In contradiction to Falta and Richter-Quittner, but in agreement with other investigators it was found that human red blood corpuscles are permeable for Cl^- . They are nearly impermeable for the sulfate ion. The anions of sulfonic acid dyes, chemically to a certain extent similar to the sulfate ion, did not penetrate the red blood corpuscles. The expts. were made with Cyanol extra (Cassella & Co.), Light green F. S. (Gruebler & Co.), Ponceau 2 R. (Hoechst) and Setopalin (Geigy). These dyes have small mols., are little absorbed, possess no marked indicator properties, and are insol. in lipoids. The Br^- behaves like the Cl^- . The phosphate ion penetrates much less than the Br^- ions. In the case of the phosphate ion it was shown that at room temp. the red blood corpuscles were much more permeable than at $2-3^\circ$ (the temp. at which all the other expts. were carried on). A strong current of O_2 was always led through the blood for $\frac{1}{2}$ hr. to drive out the CO_2 before the expts. S. AMBERG

The metabolism of obesity. FR. ROLLY. *Deut. med. Wochschr.* 47, 887-9, 917-9 (1921).—Report of 2 cases in which the gaseous exchange could be studied before and during obesity. The basal metabolism was detd. and the changes produced by food, particularly by the ingestion of a large meal of meat were also detd. In one case the obesity had shown itself 1 year after the removal of the testicles on account of tuberculosis. The wt. had increased from 56.7 to about 88 kg. In the other case the wt. was 57 kg., an exophthalmic goiter was removed. About a year later a child was born and the mother nursed it, during this time the wt. increased to 89.5 kg. The most striking feature of this case was that during obesity the O_2 consumption after a large meal of meat increased much less than before. The specific dynamic action of albuminat exceeded that of meat. S. A.

The combination of the Sachs-Georgi and Wassermann reaction. S. ROTHMAN. *Deut. med. Wochschr.* 47, 952-3(1921).—The flocculent ppt. of a Sachs-Georgi reaction gives a positive Wassermann reaction, while the supernatant fluid does not. Suitable suspensions of BaSO_4 and $\text{Cu}(\text{OH})_2$ in physiol. saline soln. also inhibit hemolysis, while the filtrates do not. The positive Wassermann reaction in the first instance may be due to physical absorption of complement, and need not mean a specific positive reaction. S. AMBERG

The influence of calcium gum solution on blood coagulation and hemorrhage. H. GOERING. *Deut. med. Wochschr.* 47, 955-6(1921).—The intravenous injection of 10 cc. of 10% CaCl_2 in 3% acacia soln. leads to a rapid diminution of the coagulation time, which diminishes so slowly that at the end of 24 hrs. the blood still coagulates decidedly more rapidly than before injection. Such injections were used in hemorrhages of various kinds with good results. S. AMBERG

The biological property of the flocculent precipitate produced in the serologic demonstration of lues. H. SACHS and H. SAHLMANN. *Deut. med. Wochschr.* 47, 1063-5(1921).—The flocculent ppt. of a Sachs-Georgi reaction contains most of the anti-complementary substance as tested by a suitable hemolytic mixt. The fluid contains some of it also. The anti-complementary property is lost on heating to 100° . S. A.

The chemical composition of the flocculent precipitate of the Sachs-Georgi reaction for the demonstration of syphilis. M. KLOSTERMANN and W. WEISBACH. *Deut. med. Wochschr.* 47, 1092-4(1921).—By far the greater part of the Sachs-Georgi ppt. is formed by lipoids. It contains only small amts. of protein and they are in the form of globulin. S. AMBERG

Artificial complement. L. v. LIEBERMANN. *Deut. med. Wochschr.* 47, 1283-4 (1921).—The artificial complement is formed by a mixt. of MeOH soln. of Na oleinate

and CaCl_2 and inactivated rabbit serum. The MeOH must be very pure and not hemolytic. Such complement can activate the hemolytic immune body (amboceptor), just as the natural can. The artificial complement is deviated by antigen-antibody systems in the Wassermann reaction as well as in glanders and tuberculosis. The artificial complement cannot replace the guinea pig serum as yet. S. AMBERG

The antigenic properties of organ lipoids. P. NIEDERHOFF. *Deut. med. Wochschr.* 47, 1284-5(1921).—The residue of alc. exts. of guinea pig kidneys was injected intravenously in rabbits. Later the rabbit serum was tested with the homologous ext. of lipoids. It did not produce a ppt., neither did it possess hemolytic properties for sheep corpuscles. Rabbits treated with aq. exts. of guinea pig kidneys gave a serum which pptd. such exts. and was hemolytic. S. AMBERG

Artificial increase of virulence of tumor transplants in mice by lactic acid. P. ROSROCK. *Deut. med. Wochschr.* 47, 1323-4(1921).—Malignant tumors of mice, which did not take in more than 33% on transplantation, took in nearly 100% when 0.5 cc. of 0.5% lactic acid free or neutralized was injected at the same time. No actual figures are given. S. AMBERG

The relation of the carbon dioxide tension of alveolar air to the physiology and pathology of the stomach digestion. F. KAUDERS AND O. PORGES. The relation of the carbon dioxide tension of the alveolar air to the chlorides of the blood serum. H. ESSEN, F. KAUDERS, AND O. PORGES. *Deut. med. Wochschr.* 47, 1416-7(1921).—After a meal the CO_2 tension of the alveolar air may increase distinctly. The main reason is the secretion of HCl into the stomach. In cases of anacidity this CO_2 increase does not occur. In other pathol. cases this relationship was evident. The mineral metabolism, particularly the Cl metabolism, affects the CO_2 tension of the blood. Increase of Cl in serum brings decreased CO_2 tension and *vice versa*. S. AMBERG

Newer results with regard to placental and eclampsia investigations. W. LIEPMANN AND SCHULZ. *Deut. med. Wochschr.* 47, 1417-8(1921).—The placenta was transfused at body temp. with 1% dextrose soln., 1% casein soln., milk in diln. of $1/10$ and lactose soln. The dextrose concn. after transfusion was $1/4-1/3$ of the original. The N of the casein soln. dropped markedly; after milk transfusion there was a reduction of the Kjeldahl-N of $1/3$, while the formol titrable N was increased 282.5%. The lactose decreased about 39%. Placenta kept 2 hrs. at 75° showed hardly any changes of either Kjeldahl- or formol-N in the transfused milk. The placenta of 3 cases behaved somewhat differently. Each showed an increase of the Kjeldahl-N in the transfusate from about 7-35%. The formol-N increased 80, 700 and 35%. The lactose content diminished about 58 and 49%. The first placenta came from a case of eclampsia, the two others from cases of imminent eclampsia. It is stated that the placenta is the place where the eclampsia toxin is formed. S. AMBERG

Destruction of the reactivity of luetic sera by formaldehyde. H. DOLD. *Deut. med. Wochschr.* 47, 1435-6(1921).—Addition of CH_2O to specially tested Sachs exts. as used for the Sachs-Georgi reaction prevents this reaction; addition to luetic serum prevents it also. This is brought in relation to the prevention of swelling of gelatin previously treated with CH_2O , by the assumption that inhibition may have something to do with the formation of the flocculent ppt. S. AMBERG

Hematic reactions to tuberculin. Importance of Arneft's neutrophile scheme. PIETRO PERONA. *Arch. farm. sper.* 34, 49-59, 65-9, 81-93(1922). A. W. DOX

The alkalimetry of whole blood. II. The acid-fixing power of the blood in renal disease. J. B. RIEGER AND H. A. FREUND. *Arch. Intern. Med.* 30, 517-30(1922); cf. C. A. 14, 2940.—The greatest amt. of acid that can be added to blood contg. 0.1% $\text{Na}_2\text{C}_2\text{O}_4$ without agglutinating the erythrocytes is a measure of the acid-binding value of the blood and is designated "oxydesis." One cc. normal blood will bind 0.9 cc. 0.01

N HCl. Values below this are an early and const. sign of glomerular insufficiency. In the diffuse nephropathies, oxydesis is definitely increased before there is retention of H_2O , Cl, or phenolsulfonephthalein and long before there is N retention. In the degenerative vascular nephropathies and in cardiorenal disease, oxydesis is not increased until the late stages.

I. GREENWALD

The supposed relation between alkalosis and tetany. ISIDOR GREENWALD. *J. Biol. Chem.* 54, 285-304(1922).—After intravenous injections of Na_2CO_3 or $NaHCO_3$ into dogs, there is a retention of CO_2 which is so great that the reaction is changed only slightly, by not more than 0.23 pH . Such change as does occur may be produced with comparatively small doses. If the injection is made sufficiently slowly to avoid apnea but is continued for a sufficiently long period, convulsions appear. Coincidentally the $BHCO_3$ content and the alkalinity of the blood begin to diminish and this process continues so that, before death occurs, both may be less than normal. The change is due, in part, to the increased production of lactic acid, which appears to begin before convulsions appear but is enormously accelerated thereafter. There is some evidence of the production of some other non-volatile acid (not β -hydroxybutyric acid). At the time convulsions appear, the concn. of Na in the plasma is the same (420-547 mg. per 100 cc.) as was observed after the injection of other Na salts (*C. A.* 13, 45). The convulsions are ascribed to "sodium poisoning" a disturbance, due to excess of Na, of the normal equil. between this and other ions. The evidence in favor of a relation between alkalosis and the tetany of parathyroidectomized dogs, gastric tetany, and the tetany of hyperpnea is examd. Only in the last named is there any indication of a change in the reaction of the blood and, even in this case, it is not the alkalosis, *per se*, but the tissue anoxemia that results from the increased stability of the oxyhemoglobin, that is the exciting factor.

I. GREENWALD

The pseudocrystalline form of gallstones. B. NAUNYN. *Deut. med. Wochschr.* 48, 1244-6(1922).—Most gallstones are round regardless of chem. compn. Some, however, have a tetrahedral or a cubical form. The surfaces of these stones usually show no evidences of rubbing. The edges are always well rounded and the interiors of the stones show a circular striation excepting toward the very exterior. The tetrahedral and cubical forms of gallstones are not truly cryst. but are produced by the pressure of the gall bladder on a mass of semisolid concretions, the innermost of which may have their round surfaces flattened by contact with the neighboring stones.

M. H.

The therapeutic use of invert sugar (calorose) particularly in cases of heart disease. FRITZ SACKI. *Deut. med. Wochschr.* 48, 1276(1922).—The invert sugar used (calorose) was obtained by hydrolyzing sucrose with dil. tartaric acid. The prepn. contains a very small amt. of unchanged sucrose. The intravenous injection of 200 cc. of a 29% calorose soln. produces no rise in body temp., raises the blood sugar only temporarily, and leads to the excretion of only a few cg. of sugar in the urine. The vol. output of urine was not increased. One liter of a 10% calorose soln. can be injected subcutaneously without irritation or other disagreeable symptoms. A calorose enema is retained well because it does not irritate the mucous membrane of the intestine. The expts. were carried out on persons afflicted with a variety of heart ailments. This preparation is recommended as preferable to glucose because of ease of preparation and cheapness.

MILTON HANKE

Concerning the chemical basis of smell in clinical diagnosis. J. KLIMONT. *Deut. med. Wochschr.* 48, 1281-2(1922).—An interesting collection of facts regarding the chemical components that are responsible for the odor of a variety of body excretions, etc.

MILTON HANKE

Observations in diabetes. HANNS HOPFNER. *Deut. med. Wochschr.* 48, 1284-5(1922).—When diabetics are injected with a small quantity of freshly drawn, citrated,

normal blood, a marked reduction in the blood sugar occurs. Blood that has been kept on ice for 24 hrs. produces the same result but to a much smaller extent. Irradiation of the liver or thigh bones of diabetics with X-rays has no effect on the blood sugar or the excretion of sugar in the urine. Irradiation of the suprarenals gives rise to a temporary increase and then to a temporary decrease in the blood sugar value. MILTON HANKE

The effect of ultra-violet light on the phagocytic action of blood serum. D. ALBELA. *Deut. med. Wochschr.* 48, 1347(1922).—Rabbits and guinea pigs with shaved ears were illuminated with ultra-violet light, 30 minutes a day, 4 days a week, over a period of 3 weeks. The concn. of opsonins in the serum, against staphylococci, was detd. before, during and after the illumination period. The phagocytic value, which varies considerably in normal animals, was unchanged by the illumination. MILTON HANKE

The production of bilirubin by the spleen. A contribution to the question of an-hepatogenic icterus. Z. ERNST AND B. SZAPPANYOS. *Klin. Wochschr.* 1, 614-5(1922).—Surviving splens were transfused for 4-6 hrs., with partially hemolyzed defibrinated blood at the rate of 4-6 cc. per min. The blood, which was originally free from bilirubin, contained 0.0005-0.002% of that substance after 4 hrs. of perfusion. The detns. were carried out according to H. van den Bergh. The presence of bilirubin was easily demonstrable, qualitatively, by the diazo test or by the method of Hammarsten and Gmelin. The pale red fatty tissue in the hilus lenis showed a marked icteric color toward the end of the perfusion period. MILTON HANKE

Anaphylactic manifestations after the injection of sanarthrite. C. H. LASCH. *Klin. Wochschr.* 1, 682-3(1922).—Sanarthrite, which is prepd. from cartilage by extn. with alc., is claimed by Heilner, it's original producer, to be free from protein. L. found that the preps. sent him gave none of the typical protein reactions. A patient with gonorrheal arthritis of the foot joint was given two injections of sanarthrite at an interval of 8 days. The first injection gave rise to no systemic effect excepting an elevation in temp. The second injection was followed by a typical, rather severe anaphylactic shock, collapse, bronchial spasm, cyanosis, feeble pulse and a temp. of 39.8°. This is believed to be a case of non-protein anaphylaxis. This is the only case out of 300, in which the injection of sanarthrite led to an anaphylactic shock. M. H.

The pathogenesis of several forms of icterus. A contribution to the question of leucine and tyrosine. A. GÉRONNE. *Klin. Wochschr.* 1, 823-32(1922).—Mixed crystals of leucine and tyrosine were found in the urine of 2 of 3 cases of acute yellow atrophy of the liver, 3 of 6 cases of severe icterus, 8 of 30 cases of catarrhal icterus, and 2 of 7 cases of gallstone colic. In mild cases of icterus either of the two amino acids may appear alone. The identity of the amino acids was established microscopically and by qual. chem. tests. MILTON HANKE

A chromodiagnosis of liver function (chromoscopy). F. ROSENTHAL AND M. FRHR. V. FALKENHANSEN. *Klin. Wochschr.* 1, 832-5(1922).—When 3 cc. of a 2% methylene blue soln. in 0.85% NaCl are injected subcutaneously into normal persons, the dye first appears in the duodenum via the bile after an interval of 55-95 min. In hepatopathies, even of the mildest type, the dye appears in the duodenum in 10-40 min. The diseased liver cells are more permeable to methylene blue than the normal cells. Two cases of prolonged hepatic duct closure are reported in which no bile was excreted into the duodenum. Methylene blue was also absent in these cases. A disease, febrile or otherwise, that is associated with a temporary derangement of the liver cells, will also lead to an increased permeability of the cells for methylene blue. In such cases the dye appears in the duodenum, via the bile, in 10-40 minutes. MILTON HANKE

A comparison of the blood pigment in health and disease. ERICH LESCHE AND KURT NEUFELD. *Klin. Wochschr.* 1, 849-50(1922).—The oxygen-binding power and the iron content of erythrocytes obtained from cases of pernicious anemia, polycythemia.

and hemolytic icterus were compared with the values obtained with normal erythrocytes. In every case 2 atoms of O were absorbed for each atom of Fe, 1.35 cc. of O₂ and 3.3 mg. of Fe per g. of hemoglobin, which is close to the theoretical figure. The blood pigment in pernicious anemia is identical with that in health. The brownish yellow color of the blood in the above diseases is caused by degradation products of the hemoglobin, such as methemoglobin, hematicin, and particularly bilirubin. MILTON HANKE

The diagnosis of pregnancy by means of a phlorhizin injection. ERICH SCHILLING AND MECHTHILD GÖBEL. *Klin. Wochschr.* 1, 889-90(1922).—The injection of 2 mg. of phlorhizin gave rise to glucosuria in 10 cases of gravidity. A similar injection into 70 normals did not produce glucosuria. Of 11 patients with a high fever, 7 developed a phlorbizin glucosuria. This test gives misleading results when applied to febrile patients. In 3 cases the Nylander test was positive when the Trommer and Heine tests were negative. It is best, when a positive Nylander reaction is obtained, to verify the result by using other tests. MILTON HANKE

Digestive leucopenia (Widal's crise hémoclasique) as a liver function test and its relation to the "green benzaldehyde reaction" in the urine. H. MEYER-ESTORF. *Klin. Wochschr.* 1, 890-2(1922).—After the normal leucocyte count has been made, the patients are given a breakfast consisting of 200 cc. of milk. Leucocyte counts are then made during the following 2 hrs. Out of 65 hepatopathies, 85% showed a marked reduction in the leucocyte count after the milk ingestion. Some of the incompletely disintegrated protein fractions, proteoses and peptones, escaped complete destruction in the damaged liver cells, and produced their typical systemic effect. The 15% of hepatopathies that failed to give a positive Widal test were afflicted with a peculiar type of icterus. They showed an initial leucopenia (3100-6200 leucocytes). The addition of *p*-Me₂NC₆H₄CHO to the urine gave rise to an intense green color. The milk diet raised the leucocyte count. These 3 characteristics always appeared at a time when the general condition of the patients was getting worse. The green coloration is not due to the presence of bilirubin. A charcoal-treated urine gives a most brilliant reaction. Any normal urine that has been freed from urobilin and urobilogen with charcoal also gives the green coloration with *p*-Me₂NC₆H₄CHO. In the presence of urobilin, a red coloration is obtained. The green coloring matter can be extd. from an acidified urine with CHCl₃. MILTON HANKE

The variation of blood sugar value after repeated ingestions of sugar under a variety of intestinal conditions, and the significance of this variation as an index to liver function. KARL TRAUGOTT. *Klin. Wochschr.* 1, 892-4(1922).—The ingestion of 20-100 g. of glucose produced a hyperglucemia of 30-50% in a well nourished man and one of 243% in the same man after 3 days of absolute starvation. The old conception that a deglycogenated liver would first restore its lost glycogen and that only the sugar in excess of this requirement was available for general cellular utilization is untenable. The ingestion of 20 g. of glucose by a moderately nourished man gives rise to the usual hyperglucemia, which has practically disappeared within an hour. If, now, a further 100 g. of glucose is ingested, there is not the slightest hyperglucemia; the blood sugar value remains constant. The same results were obtained with two hepatopathies. In another case 20 g. of glucose were ingested, then after intervals of 0.50, 2 and 3 hrs., further 20-g. portions were given, followed finally by a 100-g. portion, a total of 180 g. Only the first 20-g. portion caused a hyperglucemia. In diabetics, the ingestion of the second portion of sugar causes a hyperglucemia, excepting in cases of diabetes innocens. • The latter behave like normals in this respect. MILTON HANKE

The oxygen consumption of the erythrocytes in pregnancy. GERHARD DENECKE AND HERMANN RÜBERG. *Klin. Wochschr.* 1, 947-9(1922).—When a normal suspension of erythrocytes contg. some leucocytes is satd. with O, the container sealed and allowed

to stand for 5 hrs., a very small loss in O occurs (about 4%) that can be ascribed to the leucocytes. If the suspension contains immature erythrocytes, particularly the polychromatic variety, the loss in O on standing may amount to 75%. These immature cells are still respiring. This test was applied to the blood of 10 pregnant women. In 7 of these cases the O consumption was far greater than normal. The blood of pregnant women is in a labile condition, one in which the erythrocytes are being rapidly destroyed and replaced.

MILTON HANKE

The double immunization with euglobulin and albumin (prepared from the same blood). R. DORR AND W. BERGER. *Klin. Wochschr.* 1, 949-50(1922).—The min. sensitizing dose is larger for albumin than for euglobulin. The min. incubation time, the latent period between the time of the first injection and the time when it is necessary to reinject to get a max. effect, is longer for albumin than for euglobulin. On reinjection, the dose of albumin required to cause death is greater than that required in the case of euglobulin. In general, albumin is a far weaker antigen than euglobulin. The antigenic property decreases with increasing soly. in $(\text{NH}_4)_2\text{SO}_4$ soln. If the animal is sensitized with equal parts of albumin and euglobulin, reinjection with either antigen gives rise to the customary reaction. A sensitizing dose consisting largely of albumin produces euglobulin antibodies in the normal way, the optimum globulin reinjection dose is not reduced. If, however, the concn. of albumin in the sensitizing dose is below that of the euglobulin, the animal becomes sensitized to the euglobulin only. M. H.

The relative volume of corpuscles and plasma. J. M. H. CAMPBELL. *Brit. J. Exptl. Path.* 3, 217-24(1922).—A method is described for estg. accurately the vol. of red corpuscles in whole blood. The normal value is 40%. The corpuscular vol. varies almost directly with the hemoglobin percentage. There is little change in the concn. of hemoglobin in the corpuscle in various pathol. conditions. The term "volume index," which is the ratio of the corpuscular vol. to the number of red cells, gives a measure of the relative size of the blood cells. The size depends almost entirely on the hemoglobin content. The color index is a rough guide to the size of the av. red cell. In pernicious anemia the av. cubic content of each red cell is increased by about 30%. In secondary anemia and chlorosis it is diminished by about 30%. In polycythemia it is unchanged. The diam. of the corpuscles calcd. from the vol. agrees fairly closely with the direct measurements made by other observers. From many points of view the blood changes in chlorosis are exactly the same as in the secondary anemias, and do not resemble in any way the changes in the other so-called primary anemias. HARRIET F. HOLMES

The antitryptic action of the blood. E. BEARON. *Brit. J. Exptl. Pathol.* 5, 224-30(1922).—The albumin fraction of the serum proteins is more antitryptic than the globulin fraction; in human serum the inhibiting factor lies almost entirely in the former. This association of the antitryptic action with the albumin fraction applies also to the abnormal increment of antitrypsin occurring in certain conditions of disease. There is no proportional relation between the antitryptic power of the serum and the concn., either of the total protein or of the albumin; but, on the contrary, an increased inhibitory capacity may be accompanied by a diminished protein content, and especially by a diminished albumin content. The antitryptic power of the serum cannot be conceived as due to a simple diversion of the enzyme by the protein as such, but must be dependent upon some at present unrecognized character of this protein. HARRIET F. HOLMES

The anti-bactericidal properties of colloidal silica. S. L. CUMMINS. *Brit. J. Exptl. Pathol.* 5, 237-40(1922).—Colloidal SiO_2 interferes markedly with the bactericidal power of blood. It inhibits the action of "complement" in a hemolytic mixt. This anti-complementary property is probably the character to which it owes its antibactericidal power. These properties, together with its want of any demonstrable germicidal power, point to colloidal silica as likely to be of great use in blood cultures in bacteremia.

HARRIET F. HOLMES

Silicosis and miners' phthisis. W. E. GYR AND E. H. KETTLE. *Brit. J. Exptl. Pathol.* 5, 241-51(1922).—Insol. SiO_2 and SiO_2 sol injected subcutaneously cause similar and characteristic lesions consisting of a central area of necrosis surrounded by a zone of leucocytes; around this again is a second annular zone of necrosis limited by macrophages and granulation tissue. Tubercle bacilli proliferate rapidly in the necrotic areas, a small dose of bacilli becoming a large dose. In this way silica aids in establishing a local infection.

HARRIET F. HOLMES

A bacteriolytic substance ("lysozyme") found in secretions and tissues. A. FLEMING AND V. D. ALLISON. *Brit. J. Exptl. Pathol.* 5, 252-60(1922).—There exists in human secretions and tissues (with few exceptions), as well as in animal and some vegetable tissues, a powerful bacteriolytic agent, lysozyme. The lytic action of this substance is especially manifested on certain non-pathogenic bacteria, and in all probability it is the cause of such bacteria being non-pathogenic, but it is excreted also on some bacteria which are pathogenic to the lower animals and some which have been isolated from the human body. A large non-pathogenic coccus has been used as an indicator microbe in the investigation of the distribution of lysozyme. The lytic substance is present in secretions, especially in tears, nasal mucus, and sputum, and in tissues, especially in cartilage, and is present in large quantity in white of egg. The properties of lysozyme are detailed. Resistant forms of the indicator coccus are readily developed, and strains made resistant to one tissue are equally resistant to all tissues, indicating the essential similarity of lysozyme from different sources. Lysozyme is not absorbed by satn. with the test microbe, but on the other hand the lytic power is increased, and the increase is dependent on the number of microbes dissolved. It has not been found possible to transmit the lytic principle in series as can be done with the "bacteriophage," and a consideration of the properties of lysozyme and the bacteriophage makes it clear that there are fundamental differences between them.

HARRIET F. HOLMES

Agglutination of washed red blood-corpuscles by colloidal silica. S. L. CUMMINS. *Brit. J. Exptl. Pathol.* 5, 260-62(1922).—Colloidal SiO_2 soln. to which sufficient salt has been added to bring the mixt. up to 0.75% of NaCl brings about rapid agglutination of washed red blood-corpuscles, and this result can still be obtained after considerable diln. The flocculation and sedimentation of washed red cells by colloidal silica as above is to a great extent prevented by the presence of concd. human serum, this inhibition disappearing as the serum is made more dil. The inhibition seems to depend upon the formation of a gel.

HARRIET F. HOLMES

Serum globulin and serum albumin as anaphylactogens. E. STERN. *Arch. Hyg.* 91, 165-78(1922).—The euglobulin, pseudoglobulin and albumin fractions of horse serum were compared as to their ability to act as anaphylactogens. The euglobulin was obtained by $\frac{1}{2}$ satn. with $(\text{NH}_4)_2\text{SO}_4$ and pseudoglobulin by $\frac{1}{2}$ satn. with $(\text{NH}_4)_2\text{SO}_4$. The protein soln. remaining after pptn. of the globulins was considered the albumin fraction. The albumin was decidedly inferior to the globulins as an anaphylactogen, in that larger doses and longer periods of incubation were necessary to produce fatal anaphylaxis. The albumin fraction was not considered as an individual protein. That it contains traces of globulins was shown by the fact that animals sensitized with large doses of albumin gave reactions to euglobulin. The inferiority of this impure albumin fraction was explained by the author on the basis of the findings of Lewis (*J. Infectious Diseases* 17, 241(1915)) on the inhibitory action of mixts. of proteins on anaphylaxis.

JULIAN H. LEWIS

Uric acid content of the blood in diseases of the kidney as compared with the non-protein nitrogen and creatinine. ERICH KRAUSS. *Arch. klin. Med.* 138, 340-52 (1922).—The conception of Folin and Denis, that an increased uric acid content of the blood with a normal rest N points to a gouty diathesis, is denied. In leucemia, poly-

cythemia, poisoning with the heavy metals, heart decompensation and in many forms of diabetes, the rest N is normal while in the blood uric acid is increased. J. H. L.

Biochemical studies in ten cases of dementia precox. K. M. BOWMAN, J. P. EIDSON AND S. P. BURLADGE. *Boston Med. Surg. J.* 187, 358(1922).—No const. findings were obtained which would serve to explain dementia precox on the basis of a simple dysfunction of a single gland. There was found a tendency towards a low basal metabolism and an abnormally sustained blood sugar curve, but such findings were not const. In no case was there an increased basal metabolism nor was there a subnormal (flat) blood sugar curve. JULIAN H. LEWIS

Immunization against diphtheria in man. HANS OPITZ. *Centr. Bakt. Parasitenk.*, I Abt. 83, 262-5(1922).—The toxin-antitoxin mixt. produces an active immunization in man by the action of toxin which is released in the body from its combination with antitoxin. Slightly over-neutralized mixts. rather than highly over-neutralized mixts. are preferred. JULIAN H. LEWIS

The influence of ultra-violet rays on antihodies in vivo. P. POTTHOFF AND G. HEUER. *Centr. Bakt. Parasitenk.*, I Abt. 83, 299-306(1922).—The exposure of animals to ultra-violet rays has only a slight influence on the formation of antibodies. Pigmented animals show this influence more than unpigmented ones. However, at the height of antibody formation when the titer is somewhat const. exposure of animals to ultra-violet light causes a very great increase in the titer. This effect, however, is not permanent and the return of titer to preimmunization level is much more rapid than in the unexposed animals. JULIAN J. LEWIS

The combination of the Sachs-Georgi reaction and the third modification of the Meinicke reaction. W. F. WINKLER. *Centr. Bakt. Parasitenk.*, I Abt. 83, 375-8(1922).—The simultaneous use of the Sachs-Georgi and 3rd modification of the Meinicke reaction is an improvement which makes the diagnosis of syphilis more certain than either one alone. By their combination alone can they be used as a substitute for the Wassermann reaction. JULIAN H. LEWIS

The influence of ultra-violet light on antihodies in vitro. GEORG HEUER. *Centr. Bakt. Parasitenk.*, I Abt. 83, 380-7(1922).—Antibodies are sensitive to ultra-violet rays when dild., and are so in direct proportion to the amt. of dild. The agglutinins for cholera and paratyphoid A are less resistant to ultra-violet rays than those for typhoid. The bacteriolysins are less resistant than the agglutinins. JULIAN H. LEWIS

The thermostability of bound antibodies. WILHELM SPÄT. *Centr. Bakt. Parasitenk.*, I Abt. 83, 387-93(1922).—Typhoid bacilli possess 2 receptors for agglutinins. One of them produces fine flocculation and the other coarse flocculation. If the bacteria are boiled only the receptors responsible for the coarse flocculation are destroyed. Bacteria having all receptors satd. with agglutinins regain their ability of agglutination when boiled. This is due to a destruction and liberation of the bound agglutinins. JULIAN H. LEWIS

The resistance of spotted fever virus in emulsions of guinea pig brain. R. OTTO AND C. C. CHON. *Centr. Bakt. Parasitenk.*, I Abt. 83, 467-71(1922).—The virus of spotted fever is increased in virulence when incubated in an emulsion of guinea-pig brain. The X-19 proteus bacillus shows no such increase. JULIAN H. LEWIS

Agglutination in atmospheres of various gases. FUSAO ISHIWARA. *Centr. Bakt. Parasitenk.*, I Abt. 83, 585-9(1922).—Agglutination in an atm. of O is retarded while in N it is markedly accelerated. JULIAN H. LEWIS

The preservation of blood samples for the Wassermann test. FR. REICHERT. *Centr. Bakt. Parasitenk.*, I Abt. 83, 593-8(1922).—Sera to which trypanflavin is added in the concn. of 1:1500 can be kept for long periods of time unchanged as to their results with the Wassermann reaction. JULIAN H. LEWIS

Serum concentration and viscosity of the blood in Basedow's disease. GUSTAV DRUSCH. *Deut. Arch. klin. Med.* 138, 175-80(1922).—The viscosity of the whole blood in Basedow's disease is of little significance because of its dependence on the erythrocyte count and the hemoglobin %. On the other hand the viscosity of the serum in Basedow's diseases is on an av. 1.63 while in myxedema it is 1.94. Normally the protein content of serum detd. by its refraction lies between 7 and 9%. In 4 cases of Basedow's disease it was under 7% and in 1, it was 6.3%. The av. was 7.21%. In myxedema the av. was 9.13%. The changes in viscosity and protein content of the blood in Basedow's disease are proportional to the severity of the disease. The viscosity and protein content change toward normal with therapy.

JULIAN H. LEWIS

The urea-forming capacity of the liver in liver diseases. GEZA HETENYI. *Deut. Arch. klin. Med.* 138, 193-9(1922).—The activity of the liver to form urea was detd. by feeding NH_4 citrate and measuring the amt. of urea secreted in the urine. In all diseases of the liver the urea-forming capacity is reduced. This is especially true in atrophic cirrhosis, luetic hepatitis and catarrhal icterus. Mechanical icterus alone apparently has no effect. On the basis of these expts. a low-protein diet is indicated in liver diseases.

JULIAN H. LEWIS

Blood reaction and dyspnea in kidney diseases. H. STRAUB AND KLOTHILDE MEYER. *Deut. Arch. klin. Med.* 138, 209-28(1922).—In 21 patients with renal disease the CO_2 -binding capacity of the blood and the CO_2 tension of the alveolar air were detd. From the results the reaction of the blood was calcd. In slight renal disturbances the blood reaction was normal, lying between 7.3 and 7.4, av. 7.33. With a low CO_2 -binding capacity (hypocapnia) the CO_2 tension was decreased so low that in many cases the reaction of the blood remained normal. The hypocapnia was compensated. If the compensation was insufficient the blood reaction approached acidity. In these cases there is dyspnea.

JULIAN H. LEWIS

The significance of cholesterol in infection. ERNST LEUPOLD AND L. BOGENDÖRFER. *Deut. Arch. klin. Med.* 140, 28-38(1922).—In 20 cases of acute infection the cholesterol content of the blood decreased and then increased during the disease. During convalescence a hypercholesterolemia developed. Neither the fever nor a low diet is responsible for the hypocholesterolemia. The cholesterol is probably protective by combining with the toxins produced in infection. Animals fed with cholesterol are more resistant to exptl. infection and to intoxication with diphtheria toxin than those that are not. The presence of large amts. of cholesterol in serum has no effect on the *in vitro* growth of bacteria nor does it increase the phagocytosis of bacteria by human or rabbit leucocytes.

JULIAN H. LEWIS

Nonspecific immunity. P. F. CLARK, C. E. ZELLMER AND H. W. STONE, J. *Infectious Diseases* 31, 215-25(1922).—By the repeated injections of Gram-positive cocci, rabbits are rendered more resistant to the injection of a totally unrelated organism, *B. typhosus*. This type of nonsp. vaccination causes the rabbits to respond to subsequent inoculations with *B. typhosus*, with a formation of a higher concn. of agglutinins against this organism than do normal animals kept under the same living conditions. It is suggested that a similar nonsp. immunity may be built up in the human individual that lives in the city where there is a rich and varied bacterial environment producing, as the result, a greater resistance to disease than in the rural bred individual.

JULIAN H. LEWIS

Vasoconstrictors in the blood in hypertension. WALTER HÜLSE. *Zentr. inn. Med.* 43, 1-7(1922).—In nephritis and in essential hypertension a hyperadrenalinemia cannot be demonstrated. Serum from acute nephritis has the ability to sensitize the vessels of a normal animal to adrenaline. When an injection of adrenaline follows an injection of Ringer soln. or normal serum the rise of blood pressure is slight but when it

follows an injection of nephritic serum the rise in blood pressure is several times as great.

JULIAN H. LEWIS

The cholesterol content of blood serum. HERMAN STRAUSS AND WOLFGANG SCHUBART. *Zentr. inn. Med.* 43, 425-32(1922).—The highest values for blood cholesterol are seen in the nephroses; they often reach 500 mg. per 100 cc. blood. There seems to be no relation to the blood rest N. Icterus and other liver diseases often, but not always, show an increased cholesterol content of blood. The highest values were in carcinomatous metastases in the liver. In cirrhosis of the liver the blood values were low. In gall stones there was no increase. Diabetes showed a moderate increase. In tuberculosis the blood cholesterol is low. The location of syphilitic lesions det. the blood cholesterol value. The blood cholesterol has no relation to the Wassermann reaction. Blood diseases gave low values. In infectious diseases cholesterol is high in the beginning stages but low when the fever goes. Pregnancy shows an increased value.

JULIAN H. LEWIS

The influence of dilution with salt solution on the titration of agglutinin. GEORG HEUER. *Z. Hyg. Infektionskrankh.* 95, 100-4(1922).—Antisera to the bacteria which have good agglutininogenic ability show upon diln., a certain agglutination optimum. If this optimum is at a concn. of 1:100 or 1:200 when the diln. has been made with salt soln., the same optimum is at a concn. of 1:10 or 1:20 when the diln. is made with normal serum. This difference in the results of dilg. with normal serum and NaCl soln. is not due to the action of the NaCl, to H-ion concn. or differences in surface tension. The action of normal serum is explained as a "holding-back," a physicochem. phenomenon which is resident in the globulin fraction of the serum.

JULIAN H. LEWIS

The action of killed tubercle bacilli. H. SELTER. *Z. Hyg. Infektionskrankh.* 95, 233-44(1922).—Various preps. of killed tubercle bacilli do not produce an immunity to tuberculosis in guinea pigs. Whatever actions these preps. have are similar to the action of tuberculin.

JULIAN H. LEWIS

Anaphylaxis with the isolated organs of the frog. M. KOCHMANN AND P. SCHMIDT. *Z. Hyg. Infektionskrankh.* 95, 245-54(1922).—The vessels of a frog, injected 4 wks. previously with human serum, showed a vasoconstriction when perfused with human serum after the method of Löwen and Trendelenburg. The vessels of such an animal react no differently to the antigen than a normal. Bacterial and serum anaphylatoxins which are active for guinea pigs produce a vasoconstriction in frogs. The isolated heart of frogs that had been previously injected with serum did not react to the same serum. The heart of normal frogs did not react to anaphylatoxin. Agar-agar anaphylatoxin had no other action on isolated frog intestines than normal serum would have. Neither a nerve-muscle prep. nor muscle alone from the frog show any different action as the result of the application of anaphylatoxin which caused an anaphylaxis reaction in guinea pigs.

JULIAN H. LEWIS

The use of fresh unripened toxin in obtaining and testing diphtheria antitoxin. A. V. WASSERMANN AND M. FICKER. *Z. Hyg. Infektionskrankh.* 96, 1-16(1922).—No proof was obtained that diphtheria toxin produced by growing for 20-24 hrs. and used immediately gave any better results than toxin prep. in the usual manner. J. H. L.

The influence of protein injections on complement titer. KARL VON ANGERER. *Z. Hyg. Infektionskrankh.* 96, 25-6(1922).—Injections of casein, a proprietary prep. of casein, used in nonsp. protein therapy, did not cause variations in the complement titer of rabbit serum.

JULIAN H. LEWIS

The role of tropins and antitoxins in experimental cholera immunity. OTTO ORNSTEIN. *Z. Hyg. Infektionskrankh.* 96, 70-91(1922).—Antigens consisting of various modifications of cholera vibrios and broth cultures of these organisms produced antisera which contained varying amts. of agglutinins, complement-fixing substances, hemolysis,

tropins, bacteriolysins and antitoxins. It is believed that tropins and antitoxins have more to do with the action of anticholera serum than hitherto believed. Guinea pigs fed with cholera vibrios and tested for immunity with intraperitoneal injections of living vibrios showed not only the Pfeiffer phenomenon but also the marked development of tropins.

JULIAN H. LEWIS

The inheritance of anaphylaxis and sensitiveness to toxins. R. ORRO. *Z. Hyg. Infektionskrankh.* 96, 378-408(1922).—Young guinea pigs do not inherit anaphylaxis sensitization from sensitized fathers. The young of male guinea pigs immune to the toxins abrin and ricin are not only not immune to these toxins but are hypersensitive. The young of female guinea pigs that have been immunized to these toxins are hypersensitive if they were born after the mother's immunity had disappeared or if tested after the disappearance of the inherited passive immunity.

JULIAN H. LEWIS

Swelling measurements on human connective tissues and their bearing on M. H. Fischer's theory of acid formation in edema. H. SCHAÖR AND H. MENSCHEL. *Kolloid Z.* 31, 171-81(1922).—Fischer's fundamental work on the pathol. distribution of water in the animal tissues does not cover the connective tissues, although edema appears to originate essentially in the connective tissues. *Swelling of connective tissues.*—The human umbilical cord consists almost entirely of connective tissue; it was used in the fresh condition for the swelling expts. The chords were cut into small discs and preserved with the addition of traces of toluene. The results are shown in curves. In alkalies there is considerably more swelling than in acids. Large acid addition causes coagulation and large alkali addition causes peptization. NaCl addition causes decrease of swelling. Neutral salts influence it in accord with their relative positions in the Hofmeister series. The congenital conditions of the umbilical cord det. very largely the extent of the swelling or shrinkage. *Swelling of tendon collagen.*—Tendons consist almost entirely of fibrous collagen. When treated the same as the umbilical cord preps. they show different swelling characteristics. They also show swelling in acids and alkalies but in the reversed order of magnitude. In neutral salt solns. the tendons swell instead of dehydrate but the swelling effects of acids and alkalies are decreased by neutral salts. *Swelling of connective tissues as a whole.*—As a representative of the "whole connective tissue" subcutaneous connective tissue was employed; this consists both of connective and collagen tissues and is generally the locus of edema formation. The results, demonstrated in curves, show a decrease of swelling in general and considerably smaller differences between swelling in acids and in alkalies. The admission of the fact that two "swelling antagonists" are present makes these results intelligible. Thus in the neutral zone the whole connective tissue swells with a distinct minimum. In the case of an acute pus infection the H^+ concn. is $[H^+] = 2.5 \times 10^{-6}$, whereas the normal blood has $[H^+] = 0.45 \times 10^{-7}$. Swelling curves between H^+ concn., of 0.5×10^{-7} and 3.2×10^{-6} , show that there is a swelling minimum at 8×10^{-7} , which indicates that within the limits of acidity ever attained in the living body, there is less swelling than in the normal tissue with the normal blood acidity or H^+ concn. In neutral salts the results are somewhat irregular, yet the Hofmeister series can again be recognized. Nonelectrolytes have no effect. Swelling processes which have been observed may be the resultant of two antagonistic effects as in this case of connective tissue. Exception is taken to Fischer's theory on the origin of acidosis and edema. Edema starts in the connective tissue and a distinction should be made between edema of cells and that of connective tissue. The presence of acid in the tissue (acidosis) does not account for the swelling of the connective tissue but on the contrary, as is clinically observed, in case of high acidosis (diabetes), in the subcutaneous connective tissue there is no swelling but marked dehydration.

A. MUTSCHALLER

Experiments on anaphylaxis with azoproteins. K. LANDSTEINER. *Proc. Acad.*

Sci. Amsterdam 25, 34-5(1922).—A preliminary communication (cf. *C. A.* 12, 2373; 14, 77). Guinea pigs previously injected with an azoprotein (horse serum + arsanic acid) show anaphylactic reactions upon being reinjected with another azoprotein contg. the same group, e. g., fowl serum + arsanic acid; but they do not show anaphylactic symptoms upon reinjection with a compd. of arsanic acid and a substance of simpler compn., e. g., tyrosine. The latter substance, on the other hand, seems capable of desensitizing the animals.

W. A. PERLZWEIG

Ochronosis in alkaptonuria. W. KLEINSCHMIDT. *Frankfurter Z. Path.* 28, 73-95 (1922).—A report of the 34th recorded and 16th autopsied case, in a 66-yr.-old man, who had been alkaptonuric all his life, with resulting arthritis alkaptonuria. The pigment deposits in the cartilages were investigated in formalin-fixed material, and all were found of identical character. The pigment was insol. in H_2O and fat solvents, slightly sol. in weak acid or alkali, readily in hot 5% NaOH, only partly pptg. on neutralization. It gave no reaction for Fe. It was amphoteric, inclining toward the acid side. It gave no spectral absorption bands, did not stain with fat dyes, bleached slowly with H_2O_2 . It most closely resembled melanin in its properties, but differed in not reducing $AgNO_3$.

H. G. WELLS

Hydropic degeneration of liver cells and water poisoning of liver cells in general. B. FISCHER. *Frankfurter Z. Path.* 28, 201-52(1922).—This condition is produced experimentally by certain poisons, i. e., cocaine, pheuylhydrazine, amylene hydrate, P, As, $CHCl_3$, paraffin oil and "Granugenöl" (a special mineral oil). It is attributed to alteration of the cell lipoids which increases the cell permeability to H_2O . Lipoid-sol. poisons produced much more cellular edema than poisons not sol. in lipoids, at least in the aromatic series. With lipoid sol. basic amines (e. g., histamine) it is possible to produce edema by virtue of their affecting the lipoids of the capillary endothelium. Hunger dropsy is attributed also to loss of cell lipoids.

H. G. WELLS

Parathyroid gland enlargement in multiple giant cell sarcoma of bones. BRUNO GÜNTHER. *Frankfurter Z. Path.* 28, 295-318(1922).—The chem. interest lies in the fact that in this as well as in other bone diseases such parathyroid enlargements are often seen, probably because of the function of this organ in Ca metabolism.

H. G. WELLS

Parathyroid tumors in relation to osteomalacia. B. STRAUCH. *Frankfurter Z. Path.* 28, 319-34(1922).—S. reports 10 cases from literature of parathyroid tumors or enlargements associated with osteomalacia or other bone diseases, and adds one of his own. The relation of these growths to abnormal Ca metabolism is discussed but no conclusions are reached.

H. G. WELLS

Osteomalacia. ADOLF POSSELT. *Frankfurter Z. Path.* 28, 427-54(1922).—In the Tyrol this disease is less often puerperal than it is generally believed to be, and often is familial. Of 67 non-puerperal cases, 10 being males, there were indications of hereditary factors 20 times, often associated with endocrine abnormalities. These observations support Pommmer's hypothesis that osteomalacia is of central nervous origin, depending on a hypothetical metabolic center.

H. G. WELLS

Intracellular digestion. The enzymes and anti-enzymes concerned. F. L. OPE. *Physiol. Rev.* 2, 552-85(1922).—This discussion is limited to the enzymes of the leucocytes and the anti-enzymes which act against them. No new material. Extensive bibliography.

H. G. WELLS

Experimental studies on the production of cancer by gas-works tar. HEINZ JORDAN. *Z. Krebsforschung* 19, 39-55(1922).—J. has corroborated the work of others; in white mice treated with tar for four months or less, 100% showed either cancer or precancerous changes. When the tar was distd. at 400° the volatile fraction did not produce these changes but the residue produced the typical proliferative changes in about $1/4$ the time required with the whole tar. No proliferation could be produced with

anthracene oil. Different mice showed a marked difference in the rapidity with which they developed proliferation with the same amt. of injury by the tar. Apparently the work was not followed to a point to det. just how many of the mice with precancerous changes would have developed actual carcinoma.

H. G. WELLS

Immunity in cancer. W. CASPARI. *Z. Krebsforschung* 19, 74-100(1922).—C. lays particular emphasis on the necrosis which takes place in cancers as leading to connective tissue reaction. Injection of necrotic cancer tissue that has been heated 1 hr. at 56-59° produces a distinct resistance to inoculation with tumor tissue. Three min. at 100° destroys the immunizing agent. If a rabbit is injected with mouse tumor its serum shows an increased toxicity for mice for several weeks. The toxic substance in the rabbit serum is thermostabile. C. corroborates the work of Murphy and other Americans that increasing the number of lymphocytes by heat or X-rays increases resistance to inoculated cancers, but attributes the resistance to an immunological reaction to the tissue disintegration which accompanies this lymphocytosis. His experimental work deals entirely with transplantable tumors, and therefore the results are not necessarily applicable to spontaneous tumors.

H. G. WELLS

Action of antigen on fibroblasts in vitro. II. ALBERT FISCHER. *J. Exptl. Med.* 36, 535-48(1922); cf. *C. A.* 16, 1986.—In the immunization of fibroblasts *in vitro* against a foreign protein, there is a relation between the amt. of antigen, the time of the appearance of immunization and its duration. When a small amt. of antigen is used, immunization slowly reaches its max., and slowly decreases. When a large amt. of antigen is used, immunization reaches its max. in a short time but the protection is of equally short duration.

C. J. WHEAT

H—PHARMACOLOGY

ALFRED N. RICHARDS

Functional properties of vitamins and their significance for the pharmacological evaluation of different drugs. E. BÜRGI. *Deut. med. Wochschr.* 47, 613-5(1921).—Orypan is a commercial vitamin prepn. The influence of large doses of morphine on the respiration of rabbits can be suppressed by the administration of orypan without influencing the narcotic effect. The advantage of certain drugs or exts. of drugs over the pure active substances isolated therefrom may perhaps be brought in relation to the presence of vitamins in such exts.

S. AMBERG

The prevention of rickets in the rat by means of radiation with the mercury vapor quartz lamp. G. F. POWERS, E. A. PARK, P. G. SHIPLEY, E. V. MCCOLLUM AND NINA SIMMONDS. *Proc. Soc. Exptl. Biol. Med.* 19, 120(1921).—The effects of the radiations of the mercury vapor quartz lamp (Hanovia, Alpine type) on the growth and calcification of the skeleton of the rat, and on the animal as a whole, seem to be similar if not identical with those brought about by direct sunlight and by cod-liver oil.

C. V. B.

The effects of pituitary extract on the body temperature of animals rendered poikilothermic by destruction of the optic thalamus. F. T. ROGERS. *Proc. Soc. Exptl. Biol. Med.* 19, 125(1921).—A series of pigeons were reduced to the poikilothermous condition by first removing the cerebral hemispheres *in toto* by the scalpel and then destroying the optic thalamus with an electrocautery. The intraperitoneal injection of 0.2 to 1.0 cc. of pituitary ext. (posterior lobe—Lilly) caused a sharp rise in body temp., and when the pigeons were kept in a warm incubator heat prostration was threatened. This temp. rise persisted for 12 to 24 hrs. Frequent repeated injections lead to weakness, general prostration and death. Similar injections into controls caused no abnormal temp. reaction. In the test birds the hypophyses were apparently uninjured.

C. V. B.

Cryogenin in the urine. M. TRAMASURE. *J. pharm. Belg.* 4, 767-68(1922).—A

sample of urine changed the blue color of Fehling soln. to a moss-green in the cold. This was found to be due to cryogenin, of which the patient had taken 0.5 g. The reaction is obtained 24 hrs. after the ingestion of cryogenin and can be produced with the same intensity for 6 days. Between the 7th and 10th days, it is not so distinct and can be produced only with the urine voided during the middle of the day. A. G. DuMaz

Is asphyxia the cause of drug hyperglucemias? A. L. TATUM AND A. J. ATKINSON. *J. Biol. Chem.* 54, 331-49(1922).—The administration of CO or of NaCN to rabbits produced a marked decrease (30-50 cc.) in the CO₂-combining power of the plasma and only a slight increase (0.16-2.0 mg. per 100 cc.) in the concn. of sugar in the blood. The effect of the NaCN on the CO₂-combining power of the plasma could not have been due to stimulation of the respiration for it was also observed in rabbits receiving regular artificial respiration. Na iodoxybenzoate increased the CO₂-combining power of the plasma by about 10 cc. per 100 and the sugar content of the blood by about 35 mg. The increase in CO₂-combining power was not obtained in rabbits receiving artificial respiration, but was observed after administration of epinephrine after or with the Na iodoxybenzoate. Mixts. of Na iodoxybenzoate and of NaCN in which the stimulating effect of the NaCN on the respiratory center was entirely overbalanced by the depressing effect of the iodoxybenzoate produced a fall in CO₂ capacity, rise in blood sugar and typical cyanide convulsions. The administration of Et₂O produced hyperglucemia, generally accompanied by diminished CO₂ capacity but administration of HCl before the Et₂O did not increase the hyperglucemia nor did administration of NaHCO₃ diminish it. Et₂O produced its usual effects in double splanchnotomized and in left adrenalectomized-right splanchnotomized rabbits, indicating that the hyperglucemia was of peripheral, and not of hepatic, origin. The CO₂ capacity may be kept at a normal level after epinephrine administration by means of Na iodoxybenzoate without affecting the hyperglucemia. Conclusion: If the lowering of the CO₂ capacity after administration of NaCN or of CO is an indication of diminished intracellular oxidations, which are responsible for the hyperglucemia, the same mechanism (asphyxia) cannot be responsible for the hyperglucemia following Et₂O or epinephrine. I. GREENWALD

Morphological changes produced in trypanosomes by various drugs. P. STEFFAN. *Z. Hyg. Infektionskrankh.* 96, 263-87(1922).—The site of action of trypanocidal substances are the nucleus, protoplasm and blepharoplast. The drugs tested differ in the location of their action. There is also a variation among the trypanosomes as to the rate and manner of reaction to the drugs. JULIAN H. LEWIS

Automobile exhaust gas as a health hazard. YANDELL HENDERSON. *Boston Med. Surg. J.* 187, 180-3(1922).—The principal toxic element of automobile exhaust gas is CO. Its toxicity is increased by benzene and other gases when certain fuels are used. The following practical rule was derived: when the time of exposure is expressed in hrs. and the satn. in parts per 10,000 there will be no appreciable physiological effect when the product of the time multiplied by the satn. equals 3; when the product of time by concn. equals 6, there will be in some persons a slight effect; when it equals 9 there will be in nearly every one a distinct effect; when it equals 15 the condition is dangerous. An allowable vitiation, not exceeding 4 parts of CO in 10,000 of air, is, therefore, recommended as a practical standard for vehicular tunnels. The inhalation of O-rich air is the treatment for CO poisoning. JULIAN H. LEWIS

The action of adrenaline on the circulation. A. HOLT. *Deut. Arch. klin. Med.* 138, 257-89(1922).—Adrenaline causes an increased blood pressure chiefly because of a vasoconstriction of the small arteries, especially those innervated by the splanchnics. But the large arteries of the extremities undergo vasodilatation as the effect of adrenaline. With the increase of systolic blood pressure there is sometimes a decrease of the diastolic pressure. When the aortic valves are insufficient and a part of the blood flows back into

the left ventricle in diastole, the diastolic pressure falls especially. The vasoconstriction of the small peripheral arteries increases the vol. of the blood going to and leaving the right heart. This increased vol. of blood produces an increased vol. of the lungs as the result of adrenaline injection.

JULIAN H. LEWIS

A review from the field of pharmacology. CARL BACHMANN. *Zentr. inn. Med.* 43, 201-12, 393-405, 585-92, 601-7(1922).—The period covered is Oct. 1921 to June 1922.

JULIAN H. LEWIS

Reaction of blood pressure to adrenaline in hypertension. ESKIL KYLIN. *Zentr. inn. Med.* 43, 329-31(1922).—In hypertension where there is acute nephritis the blood pressure rises after the injection of adrenaline. In hypertension with benign nephrosclerosis there is a fall in blood pressure after adrenaline injection.

JULIAN H. LEWIS

The Mechanism of specific poisons. PETER BERGELL. *Z. physiol. Chem.* 121, 231-9(1922).—When mice receive about 5 injections of tropic acid at short intervals (usually 1 day) and finally a single injection of tropine, death or illness results. The same end is accomplished by preliminary treatment with tropine followed by tropic acid. If the initial injections of tropine or tropic acid are several days apart a considerable degree of resistance to the second compd., whichever it may be, develops.

R. L. STEHLÉ

Metabolism of lipids and fats in the liver cells of fasting and phosphorus-poisoned animals. I. SALVIOLI AND I. SACCHETTO. *Frankfurter Z. Path.* 28, 111-30, 131-40 (1922).—P poisoning produces a marked fatty degeneration in the liver of animals starved to the last degree; this contradicts the negative results of other observers. Fasting dogs show a loss of neutral fats in the liver cells, but the stainable lipid droplets increase in number. Guinea pigs die before the natural fat depots are completely exhausted, but their livers show numerous cells with marked lipid infiltration. Dogs poisoned with P, when emaciated, show in the liver cells an accumulation of neutral fats not observed in fasting alone, added to the usual lipid deposit; in normal dogs P poisoning produces only neutral fat accumulation in the liver. Normal guinea pigs poisoned with P show in the liver both neutral fat and lipid droplets. This difference between the two animals is explained by the presence of lipid droplets in some of the normal guinea pig liver cells. If normal guinea pigs are poisoned with P by subcutaneous injection one does not observe the lipid increase which follows oral administration of P, or which occurs in fasting guinea pigs however the poison is given, hence it is deduced that P given by mouth so injures the alimentary tract that lack of absorption results leading to a condition of starvation. The above work was all done solely by microchemical methods.

H. G. WELLS

I—ZOOLOGY

R. A. GORTNER

Glycogen content of certain invertebrates and fishes. L. G. KILBORN AND J. J. R. MACLEOD. *Quart. J. Exptl. Physiol.* 12, 317-30(1920).—By Pfüger's method, the following glycogen percentages were found in the (moist) digestive glands (hepatopancreas): Asteroidea 0.232 to 1.52; Lamellibranchiata 0.31 to 1.56; Crustacea 0.05 to 1.39; Elasmobranchii 0.0 to 0.21; Teleostomi, 0.0 to 0.5. Feeding conditions and season seem partly responsible for the varying amts. In the (moist) muscles the following glycogen percentages were found: Lamellibranchiata 0.077 to 2.67 (the latter in the adductor muscles); Crustacea trace to 0.36; Elasmobranchii 0.0 to 0.018; Teleostomi 0.0 to 0.29. In all cases when it was possible to obtain a sufficient amt. of heart muscle, the glycogen content was found to be several times greater than that of other muscles, and sometimes greater than that of the liver; thus in the lobster 0.85-1.42% was found in the heart, while the muscle content was 0.36%. In several cases the glycogen was found to yield

a yeast-fermentable sugar after hydrolysis. In other cases part of the reducing material seemed to consist of other substances. C. V. B.

Reducing substances in the circulating fluids of invertebrates and fishes. R. S. LANG AND J. J. R. MACLEOD. *Quart. J. Exptl. Physiol.* 12, 331-7(1920).—Body fluids of Echinodermata and of Mollusca contained little or no reducing substance. Of the Crustacea, *Cancer* showed 0.039 to 0.081%, while *Homarus* had only minute traces or none at all. The difference is possibly one of feeding. In the fluids from several specimens of the dog fish (*Squalis sucklii*) no reducing substance, or traces only could be detected, except in 1 case where 0.038% was found by the picric acid method. Several of the fish were examd. immediately after being caught, so that it is unlikely that starvation is responsible for the low values. In *Clupea* and in the carp (representing the Teleostomi) the percentage of reducing substance in the blood was found to be similar to that of mammalian blood (0.071-0.145%). Reduction was detd. by the Myers-Bailey modification of the method of Lewis and Benedict and, when vol. permitted by the colloidal iron and Bertrand methods. C. V. B.

The effect of experimentally induced changes in consistency on protoplasmic movement. ROBERT CHAMBERS. *Proc. Soc. Exptl. Biol. Med.* 19, 87-8(1921).—The protoplasm of an ameba exists in a certain normal state of consistency from which it may deviate so as to solidify or liquefy. The less solid phase may be induced by agitation with a micro-dissection needle. A resting ameba has many slender pseudopodia and is relatively solid. Agitation, if slight, causes a liquefaction of the ameba and retraction of the pseudopodia which are later protruded in a broad lobate form; if extreme the cell becomes spherical, peripheral currents of granules flow from its anterior end and central currents flow forward, the cell does not move, recovery does not take place, the flow of the currents gradually slows and the animal dies. Solns. of HCl and of NaOH injected into the living ameba vary the setting time of the protoplasm; in acidified cells the peripheral backflow is quickly arrested as the surface solidifies; the result is long slender pseudopodia; alkalinized protoplasm sets slowly and the pseudopodia are broadly lobate. C. V. B.

The unusual action of Mödinger potable water on salamander larvae. K. HORMANN. *Naturwissenschaften* 10, 925(1922).—Further quant. data are given confirming previous results (cf. C. A. 16, 2368) on the action of CaCl_2 , K_2HPO_4 , K_2CO_3 , MgSO_4 and MgCl_2 solns. on salamander larvae. A larva grew normally in a K_2SO_4 soln. (1 g. per 750 cc. H_2O). C. C. DAVIS

The chemical sense of some polychaetes. HANS SCHMIDT. *Biol. Zentr.* 42, 193-200(1922).—S. studied the reaction of various parts of the bodies of *Arenicola piscatorum*, *Nereis pelagica* and *Nephtys hombergi* to stimulation with chem. irritants: solns. of sucrose, saccharin and of quinine bisulfate. He found that these animals possess a chem. irritability which is not localized but is spread in the entire epidermal layer. The anterior end reacted more strongly than the trunk or the posterior end, and the latter reacted more strongly than the trunk. Halved animals possessed a marked irritability which again was more pronounced in the anterior end. W. A. PERLZWEIG

The reaction of organisms to external stimuli. FRIEDRICH ALVERDES. *Biol. Zentr.* 42, 218-22(1922).—A theoretical discussion. W. A. PERLZWEIG

Organic regulation. II. Involution of the frog-larva tail. H. C. VAN DER HEYDE. *Biol. Zentr.* 42, 419-28(1922); cf. C. A. 15, 2510.—An extension of the studies of W. Morse (C. A. 12, 1399) on the role of autolysis in the atrophy of larval tissue in the frog. Supporting the autolysis theory H. observed an increase in the H concn. of the tail tissue accompanying its atrophy. No increase in total N in the urine was found. A large proportion of the total N is excreted in the form of NH_3 at all stages of metamorphosis. This is interpreted as indicating the deamination of tail tissue protein. While the

fat content of the tail was high, no increase in the total fat content of the rest of the body was observed with the progress of tail atrophy.

W. A. PERLZWEIG

The permeability of chitin in osmotic processes. H. EIDMANN. *Biol. Zentr.* 42, 420-35(1922).—Thin chitin membranes were found to be permeable to biol. diffusible substances, the permeability being inversely proportional to the thickness of the membrane. Thus the chitin membrane lining the anterior and posterior ends of the digestive tract of the roach (*Periplaneta orientalis*) offers no resistance to the absorption of digestion products. The crop of the same roach is lined with a very thick chitinous layer which is quite impermeable. Similarly in the olfactory organs of insects the nerve endings receive stimuli through a thin chitin membrane.

W. A. PERLZWEIG

Quantitative biology of ants. ROBERT SUMPER. *Biol. Zentr.* 42, 435-40(1922).—An interesting study of quant. relationships in the secretion of poison, HCOOH, temp. factors in relation to activity and in the mechanism of orientation in space, was made on several representative species of ants. Only the *Camponotinae*, ants without a sting but provided with a cushioned poison app., contain and secrete HCOOH. The *Myrmicinae* and *Dolichoderinae* do not secrete any acid, likewise the males of all species possess no poison app. and do not secrete HCOOH. In the *Camponotinae* no other free acid aside from HCOOH was found. The concn. of HCOOH in the secretion of *Formica rufa* varies between 21.5 and 72.3%, the content in the bodies varies between 2.8% for *Formica rubifarbis* and 18.0% in *Formica rufa*. van't Hoff's temp. coeff. holds well in regard to speed of locomotion, secretion of poison and its combative activity of various species. Thus Q_{10} for locomotion was found to be 2.17 and 1.63 for temp. intervals 11-19° and 19-28°, resp.; for HCOOH secretion 2.16, etc. Under certain conditions of space orientation it was found that reaction to light outweighs and hinders reactions to olfactory sensations.

W. A. PERLZWEIG

Causes of animal coloration. VI. The color modifications of the walking stick, *Dixippus morosus* Br. et Redt. H. PRZIBRAM AND L. BRECHER. *Arch. Entwickl. Organ.* 50, 147-85(1922).—The permanent color difference of the adult insect is not brought about by the wandering of pigment granules, but depends upon the different quant. relationships of a dark-brown melanin, a green and an orange-red lipochrome. The predominance of a particular color type depends on the illumination. A comparison is made with the development of color in the pupa of *Pieris brassicae* (*C. A.* 16, 3345). Methods of prepn. of the press juice which gave the various color reactions are included.

CHAS. H. RICHARDSON

The structure of the plasma of amebas in view of the alveolar theory (of protoplasmic structure). H. GIERBERG. *Arch. Entwickl. Organ.* 51, 150-250(1922).—The plasma of amebas is composed of numerous colloidal substances partly mixed and partly sepd. from one another. Since the H₂O content of the plasma and its soln. in H₂O change greatly, all conditions are present to permit it to appear either as an apparently homogeneous liquid, an emulsion or a foam. The views of other authors are discussed.

CHAS. H. RICHARDSON

Method of selective coloration of the nervous system in certain invertebrates. MARC ROMIEU. *Compt. rend.* 175, 455-8(1923).—A pinch of benzidine is added to a tube of distd. water acidified by a trace of AcOH. After 30 min. contact, the soln. is filtered. Previous to this the animal or a small cutting to be tested (*Phyllodoce*, *Eulalia* or the Aphroditian *Lepidonotus squamatus*) is carefully washed in distd. water and is now immersed in the benzidine bath for 30 to 60 min. A blue line*corresponding to the nervous chain appears when a drop of 12 vol. H₂O₂ is added. The animal is then examd. between the slide and cover glass in a drop of the oxygenated benzidine mixt. In a few min. the whole nervous system including the ganglia, the organs of sense, and most slender nerves can be seen. This method of nerve coloration is applicable to specimens

after alc. fixation, the color remaining for 2 or 3 hrs. when it turns brown and disappears.

L. W. RIGGS

12--FOODS

W. D. BIGELOW AND A. E. STEVENSON

The chemistry of foods and condiments in 1919-21. ED. BAIER. *Chem.-Ztg.* 46, 705-6, 725-7, 750-1, 813-5, 837-40, 890-1, 905-7(1922).

Interesting substitutes for food products. ARNO VIEHOEYER. *Am. Food J.* 17, No. 1, 21-24(1922).—Little known food and drug plants are described which are thought can supplant some products now in use. The subjects are zamia and its starch; tepary beans, a plant closely related to the common bean and lima bean; robusta coffee; the fruit of *Solanum macrocarpum* as a substitute for tomatoes; African sorrel, a spinach substitute; cassina, a tea and coffee substitute; Spanish thyme; several cubeb substitutes; and twin leaf, a substitute for goldenseal. H. A. LEPFER

Relations between the calorific values of foods determined by combustion and those determined by calculation from their chemical composition. J. KÖNIG AND J. SCHNEIDERWIRTH. *Berl. klin. Wochschr.* 58, 1103(1921); *Bull. office intern. d'hyg. publ.* 14, 1293-5(1922).—Comparison is made between the values obtained by drying and burning foods in the Langbein calorimeter and by analysis and calcn., using the following values: protein 5710 cal. per g.; fats 9,300 cal.; carbohydrates 4000 cal.; cellulose 4232 cal. (the exact value for pure cellulose is 4185 cal., but crude cellulose contains lignin and cutin which have a higher calorific value). For proteins the crude proteins are detd. and also those which are pptd. by Cu (OH)₂ (pure proteins) thus excluding amino acids, and bases which have a calorific value more nearly approaching that of carbohydrates. The results by the calcn. method are claimed to be sufficiently exact for most purposes. JACK J. HINMAN, JR.

Food value (vitamins) of cow milk in its commercial forms. FOLET AND R. LSCOCQ. *Oeuvre nationale de l'Enfance* 3, 765(1922); *Bull. office intern. d'hyg. pub.* 14, 1129(1922).—The presence or absence of antiscorbutic vitamin C is considered. Milk just brought to boiling or milk pasteurized at 74° is antiscorbutic. The property is lost on continued boiling or on keeping. Sweetened condensed milk retains more of its antiscorbutic properties than unsweetened condensed milk or evapd. milk. The Merell-Soule spray process yields a less antiscorbutic product than the Just-Hatmaker cylinder process. Fruit juices are advised for all children using condensed milks. JACK J. HINMAN, JR.

The spoiling of milk. WILFRED SADLER AND M. J. MOUNCE. *Creamery & Milk Plant Monthly* 11, 65-70(1922).—Milk clot is considered from the standpoint of the bacteriol. flora causing it and the rate of its formation as controlled by temp. Organisms present in the milk when drawn under sterile conditions from the udder are important in producing the clot, especially in connection with the subsequent peptonization of the clot. H. F. Z.

Yeast and mold counts and their relation to pasteurization of cream for butter-making purposes. B. A. STIRRY. *J. Dairy Sci.* 5, 362-71(1922).—The yeast and mold content may be reduced to a small no. in the cream by pasteurization, whereas the butter may show an increase, due no doubt to contamination in subsequent handling of the cream. The churn may be one of the greatest sources of contamination. A starter, if used, has little effect as source of yeasts and molds in final butter except in rare cases when an extremely inferior grade of starter is added. The yeast and mold counts of finished butter cannot be taken as an efficiency index to pasteurization of the cream nor considered as an effective method for detg. if raw or pasteurized cream has been used. If a standard of 30 colonies is set as the max. count of finished butter,

the count can be considered as an index of the efficiency of whole butter-making process.

H. A. LEPFER

Actinomyces in milk with special reference to the production of undesirable odors and flavors. C. R. FELLERS. *J. Dairy Sci.* 5, 485-501(1922).—Actinomyces are often present in market milk constituting about 2.5% of total organisms present. Principal means of entrance to milk are hay, straw, grain, soil, and dust raised from these materials. They may cause development of a characteristic obnoxious bitter and moldy taste for which "actinomyces odor and taste" is suggested as a descriptive term. The 2 most active species out of 11 identified were *A. griseus* and *A. albus*. These organisms grow readily in milk and are able to produce profound changes in casein and whey. Actinomyces may cause stale, musty and moldy odors in other foods. They occur in foods with molds, especially those in dried condition. Synthetic media with long low-temp. incubation should be used in isolating them from foods or other materials. A complete description of *A. griseus* Krainsky is given. H. A. L.

The influences of certain factors on the methylene blue reduction test for determining the number of bacteria in milk. E. G. HASTINGS, AUDREY DAVENPORT AND W. H. WRIGHT. *J. Dairy Sci.* 5, 438-54(1922).—The methylene blue reduction test seems to meet the need for some simple and inexpensive method for the bacteriol. analysis of milk. A review of the literature and a study of influencing factors were made. Differences in reduction time when dyes of foreign or domestic sources were used were of no practical significance. Impurities which may be present in grades which should be used are so dil. as to have no effect. The age of the methylene blue soln. appears to have no effect. There seems to be no reason to deviate from the accustomed temp. (38°) in making the tests. In general a series of samples will be placed in the same order by the reduction test no matter what temp. is employed. There is every reason to believe that every organism growing in the milk assists in the reduction of the dye but all do not function in the same degree. The test depends on the vital activities of the cells, as is shown by the effect of heating the milk to relatively low temp. or of antiseptics. The reaction of any sample of milk to which the test would be applied in practice would not be such as to interfere. Agitation of the milk has practically no effect on reduction time. The relations which may exist between diff. groups of bacteria are discussed and data are presented to illustrate their effect in influencing the reduction time. Results indicate that the reduction test will reflect only in a general way the keeping quality of milk. On account of the great complexity of bacterial flora in milk it seems impossible for the keeping quality to be detd. by any one test or probably by any group of tests. Dil. one part stock soln. (medicinal methylene blue 1 part, H₂O 2000 parts) 10 times with H₂O. Do not filter. Add 1 cc. to 10-cc. samples in tubes of the same diam. of such size that 11 cc. does not more than half fill them. The tubes should be clean and steamed; they need not be sterilized. The pipet should be rinsed 3 times with boiled H₂O between samples. After addition of the dye close the tube with the thumb or palm and invert 1 or 2 times. Wiping the moistened area of hand with clean towel will prevent contamination between samples. Place in a H₂O bath at 38°. Observation after a 6-hr. period is seldom necessary. A discussion on reading the test is given. H. A. LEPFER

Weinzirl anaerobic spore test for determining manurial pollution of milk. J. R. HUDSON AND F. W. TANNER. *J. Dairy Sci.* 5, 377-82(1922).—Examn. of over 100 samples of milk, as delivered to the creamery, showed that there is no correlation between the anaerobic spore tests as outlined by Weinzirl (*C. A.* 9, 3107) and the amt. of dirt in the milk or the no. of bacteria as detd. by the Frost plate count. The test it seems cannot be accepted as a method for accurately detg. manurial pollution of milk.

H. A. LEPFER

The relationship between the hydrogen-ion concentration and the bacterial count of commercial milk. R. W. SCHULTZ, ALBERTA MARX AND H. J. BRAVERMAN. *J. Dairy Sci.* 5, 383-7(1922).—A continuation of previous study (*C. A.* 15, 1359). Pooled milk obtained from 2 city dairies and one dairy farm. Enormous increases in bacterial count may go with slight increases in H ion concns. The differences found between lowest and highest count at various p_H readings are discussed. The results indicate that quality of market milk can be estd. with reasonable accuracy by measuring its p_H . H. A. LEPPER

The physical analysis of dry milk. R. M. WASHBURN. *J. Dairy Sci.* 5, 388-98 (1922).—A discussion of the exam. of powd. milk by phys. means giving the interpretation to be applied to the color, texture, odor, taste and soly. The significance of the cream rising, including the double coloring test of the reconstructed milk, is discussed. A microscopical study of the differentially stained powder grains is probably the most interesting feature in the phys. analysis of dehydrated milk. H. A. LEPPER

The determination of amino nitrogen and ammonia in cream and butter. L. W. FERRIS. *J. Dairy Sci.* 5, 399-405(1922).—Picric acid used with AcOH in prepg. samples of milk, cream, buttermilk and butter for the detn. of N reacting with HNO_3 in Van Slyke's app. as an index of proteolysis gives easy and rapid sepn. of proteins and other complex substances from lower degradation products, principally amino acids, reduces hydrolysis of proteins to a min. during analysis and allows holding the filtrate a reasonable time without change after prepn. of the sample for analysis. For cream add 5 cc. of 10% AcOH and 30 cc. satd. picric acid soln. to 15 g. in a 100-cc. flask, shake $1\frac{1}{2}$ hr. (or at intervals for 2 hrs.) filter on a dry filter and det. reacting amino N in Van Slyke's app. using a large bulb and a 10-cc. gas buret. For butter weigh into a 250-cc. hottle 100 g. in such consistency that it can be poured and yet have no sepn. of fat and curd. Fill with petr. ether (b. below 55°) warmed to a few degrees above room temp., shake, centrifuge and siphon off, leaving a compact mass in the bottom. Treat the residue as for cream. The amino N and NH_3 expressed as % of total N in 14 samples of fresh butter from sweet cream ranged from 0.9 to 2.3 with an av. of 1.4. When the amino N in a sample of cream or butter is used as an index of the quality of the sample, this method more nearly represents the amt. actually present. H. A. LEPPER

The copper content of cow milk. G. C. SUPPLEE AND B. BELLIS. *J. Dairy Sci.* 5, 455-67(1922).—The K Et xanthate method of Scott and Derby, which is detailed, was found to be the most satisfactory for detn. of small amt. of Cu in normal milk. It is delicate and reliable to 0.005 mg. Other methods were successful for detection. In 23 samples of freshly drawn milk 0.2, 0.52 and 0.8 mg. per l. were found as min., av. and max., resp. Pasture or stall feeding appears to have no effect. Cu in milk can be measurably increased by storing or heating in presence of the metal. Passage through copper from which Sn is worn increases Cu content slightly but not as much as would result from formation of Cu compds. around brass or bronze fittings as a consequence of poor sanitary practices. "The presence of Cu in milk, particularly when taken up as extraneous contamination, may prove to be significant in connection with the high susceptibility of the antiscorbutic vitamin to oxidation." H. A. LEPPER

Estimating added water in milk. FRITZ KOPATSCHEK. *Anales soc. quim. Argentina* 10, 74-86(1922).—Various methods are discussed. K. considers the following method very reliable and easy to carry out: To 20 cc. of the milk sample add 30 cc. uranyl acetate soln. (1.75%) and 30 cc. distd. H_2O . Shake and filter. In 10 cc. of filtrate det. Cl by titration with 0.01 N $AgNO_3$ and in the remainder lactose by polarization. Calc. the Cl and lactose (L) content of the original sample. Then $100 [K - (L + 44Cl)] / K$ = % added H_2O when K equals the av. $L + 44Cl$ value of pure samples of normal milk from the same locality. L. E. GILSON

Measuring the volume of cream on milk. H. A. HARDING, F. W. KELLY AND E. S. CURRIER. *J. Dairy Sci.* 5, 463-78 (1922).—Fill round-bottom tubes 1 in. in diam. to a depth of 204 mm. with the sample; cool in ice H_2O and store 20 hrs. at 40° F. Measure the cream layer in mm. Each mm. represents 0.5% cream by vol. Vol. measured this way agrees closely with that developed in milk bottles under similar temp. conditions.

H. A. LEPPER

Comparison of A.P.H.A. and milk powder agars. H. F. ZOLLER AND SYLVIA M. EATON. *Ice Cream Trade J.* 18, 59-61 (1922).—Milk powder agar made by a simplification of Ayer's method furnishes a regularly higher total count on market milk than does the standard agar. This difference is expressed as the A.P.H.A. agar coeff. and is obtained by the ratio M.P.A./A.P.H.A. The essential difference from Ayer's prepn. is the use of Bacto nutrient agar in place of washed agar, and also the addition of small quantities of Na citrate to render the agar and milk salts more stable towards the autoclaving temps.

H. F. Z.

Fat obtained from the milk of Egyptian goats. A. AZADIAN. *Bull. soc. chim. Belg.* 31, 171 (1922); *J. Soc. Chem. Ind.* 41, 563.—Analyses of 104 samples of goat milk gave the following max., min., and mean values, resp., for total solids 16.55, 10.65, 12.54; for fat 7.35, 2.45, 4.04; and for solids not fat 9.95, 7.60, and 8.50%. Six samples of goat milk butter also were analyzed.

WM. STERICKER

The water content of margarine. KURT BRAUER. *Chem.-Ztg.* 46, 834 (1922).—Results on samples taken from one place in margarine especially when in cube form are not reliable. An av. sample must be taken. That less H_2O is found in the outer layer is probably due to contact with the wrapping paper, which absorbs it. H. A. L.

Detection of hardened vegetable fat in lard. W. MÜLLER. *Mitt. Lebensm. Hyg.* 13, 208-17 (1922).—Reactions based on color, usual constns. and tests for Ni were found to be of no value in the detection of hardened vegetable fat in lard. The method considered the best, although not rapid, is a combination of Bömer's methods based on m. p. of phytosteryl acetate (*Z. Nahr. Genussm.* 4, 1070) and on diff. in m. p. of various glycerides (*C. A.* 8, 1174, 2433).

H. A. LEPPER

Examination of alimentary pastes for artificial color. E. ARBENZ. *Mitt. Lebensm. Hyg.* 13, 201-8 (1922).—The failure of the methods in use to detect artificial coloring in yellow Italian pastes free from egg and the difficulty of detecting coloring in pastes made from naturally yellow flour led to this investigation. A method based on that of Swiss Lebensmittelbuch is proposed. Add 40 cc. 50% alc., to 20 g. of broken paste (not ground) in a flask, warm 15-20 min. with occasional swirling on the H_2O bath. A yellow ext. shows the use of naturally colored flour or artificial color. Cool, filter, add 1 cc. 10% tartaric acid soln. and a piece of woolen thread and evap. to dryness. Wash the wool in hot H_2O and dry on filter paper. Yellow on the wool is due to artificial color.

H. A. LEPPER

Use of pectin in jams and jellies. H. S. PAINE. *Am. Food J.* 17, No. 3, 11-13 (1922).—The nature and properties of pectin are discussed with consideration of the problems involved in jelly making. The alc. pptn. method for *delg. pectin* may not give concordant results when used on diff. fruits on account of pptn. of other substances. Jellying quality may vary with diff. pectins.

H. A. LEPPER

Yield and quality in Hubbard squash. M. B. CUMMINGS AND W. C. STONE. *Vermont Agr. Sta. Bull.* 48, 222 (1922).—Good-quality squash contained on a dry basis from 10.5 to 11.7% protein, av. 11.4%, while the poor ranged from 10.8 to 15.9%, av. 12.8%. Squashes with better eating qualities as compared with the poorer carry less ash and less crude protein. Immature squashes contain more water and crude protein in dry matter than do the mature specimens.

J. J. SKINNER

The chemistry of tea. V. Tannin in manufactured tea. C. W. TRIGG. *Tea*

Coffee Trade J. 43, 684-6(1922).—The tannin content of com. teas is considered with particular reference to the source of the teas and the relation between the % tannin and the value of the teas. The effect of the nature of water upon tannin extn. is briefly treated. C. W. T.

The frozen-egg industry and the public health. BORDAS. *Rev. hyg.* 44, 613(1922).—A review of the technology, conditions of production and preservation. Frozen eggs should be received in cases with seals intact; if steam comes into contact with the case, it should be quickly condensed, a layer of frost being given; guaranty that the case has not been thawed and re-frozen should be demanded and when received the eggs should at once be placed in cold storage and kept there until used.

JACK J. HINMAN, JR.

Quality of the (French) wheats of the 1921 harvest. J. BOUYER. *Ann. fals.* 15, 332-7(1922).—Twenty-one analyses (moisture, protein, starch fat, ash, fiber, wt. of 1 grain) are given. The following method was used for starch detn.: Treat 1 g. of sample in a 250-cc. flask with a mixt. of 100 cc. of water, 1 cc. of H_2SO_4 , and 10 g. of $KHSO_4$. Insert a 50-cc. pipet in the neck of the flask and boil gently for at least 4 hrs., agitating from time to time, especially at the beginning. Cool, nearly neutralize with $NaHCO_3$, transfer to a 200-cc. flask, make up to vol., filter, clarify 100 cc. of the filtrate with 10 cc. of Pb subacetate, filter, and titrate the filtrate with Causse-Bonnans liquor following the directions of the authors very closely (adding 4-5 drops at a time and boiling vigorously after each addition). Crude fiber was deld. on the residue from the starch detn., after washing and treating with 10% potash (probably K_2CO_3 is meant—ABSTR.). The influence of proper selection and cultural methods is discussed, to show that France can grow wheat equal to other wheats. A. P.-C.

The extraction of flour from wheat and the use of substitute flours in bread making. ARPIN and FLEURENT. *Ann. fals.* 15, 362-8(1922).—The degree of extn. of flour is the amt. obtained by milling 100 kg. of wheat. Owing to variations in the quality and compn. of various wheats, the same degree of extn. would not give a uniform flour. Moreover, the degree of extn. cannot be detd. from the characteristics of the flour. In order to obtain the max. amt. of flour, A. and F. suggest establishing a standard grade by milling the best wheat under the most favorable conditions and taking everything suitable for breadmaking. This would be known as "whole wheat" flour, and it would be forbidden to make flour whiter than this standard, which would be renewed, say every 3-4 months. Of the substitutes grown in France and its colonies (rye, barley, maize, buckwheat, and rice), rye (up to 10% but preferably 6-8%) and buckwheat (about 10%) can be used, the others being unsuitable. A. P.-C.

The sanitary control of the shell-fish industry. G. BORNE, F. DIENERT, and G. HINARD. *Off. sci. tech. pêches marit. Bull.* No. 10 (Dec., 1921); *Bull. inst. Pasteur* 20, 468(1922); *Bull. office intern. d'hyg. publ.* 14, 992(1922).—A discussion of chem. and bacteriol. examn. of sea water and shellfish. Greatest emphasis is placed on *B. coli* detns., yeast-phenol bouillon being used for preliminary growth of the *B. coli* group organisms. JACK J. HINMAN, JR.

By-products of industrial abattoirs: modern butchering installations and the utilization of animal blood. "A. B." *Rev. gen. froid ind., frigorifiques* 1922; *Cuir* 1922, 281-7(1922).—Animal waste and carcasses are treated in an autoclave with steam under 4 atm. pressure at 150°. Grease passes to a neighboring grease separator, while the degreased gelatinous broth passes to an evaporator where it is evapd. and dried *in vacuo*. No steam is led directly on to the carcasses, the water in these being evapd. by a special steam heater mounted in a perforated drum. The yield from whole carcasses averages 12% fat, 22% meat meal of 7.5-8.5% N, and 13% gelatin of 9% N. Blood is placed in a cooking vessel and live steam blown in. Water is expressed from

the pasty mass by pressure and the coagulated blood is finally dried *in vacuo*. The blood meal so produced averages 13% N.

F. L. SEYMOUR-JONES

A new method of conserving feeds rich in sap and its meaning to agricultural practice. W. VOLTZ. *Landw. Ztg. Fühlings*. 71, 161-77(1922).—A general discussion of ensilage practice.

F. M. SCHERTZ

Investigation of the fodder value of straw hydrolyzed by different methods. V. Hydrolysis of straw by means of caustic soda and caustic lime in the cold (Beckmann methods). F. HONCAMP AND E. POMMER. *Landw. Vers. Sta.* 99, 231-66(1922).—Loss in crude and digestible nutrients is greater with NaOH than with the $\text{Ca}(\text{OH})_2$.

F. M. SCHERTZ

Drying foods. E. NISHINA. *Brit.* 185,725, Aug. 4, 1922. Foods to be dried are forced under pressure from nozzles on to the surface of an endless traveling band of absorbent material, such as felt, cotton fabric, etc. The band is passed through a drying chamber under reduced pressure, and the dried material is afterwards scraped from it. The treatment may be effected in an atm. of CO_2 or other inert gas.

Pectous materials. F. G. BEYLIK AND N. W. SCHWARTZLOSE. *Brit.* 184,081, Sept. 5, 1921. See U. S. 1,393,660 (C. A. 16, 448).

13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

The economic situation of the chemical industry (in Germany) in 1921-22. C. DUISBERG. *Z. angew. Chem.* 1922, *Chem. Ind.* 653-60.

E. H.

Alcohol and ether distillation. STEPHANE MASPARAUD. *Sugar* 24, 448-50(1922).—A discussion of the laws governing the sepn. of volatile substances by raising or lowering the b. p.

C. H. CHRISTMAN

Numerical values of some constants used by the refrigerating engineer. F. G. KEYES. *Am. Soc. Refrigerating Eng. J.* 8, 505-8(1922).—The most authoritative value for the abs. temp. of melting ice is 273.15°, obtained from data on N_2 , H_2 and He. Henning and Heuse's results of 273.20° is too divergent from others to be considered final.

H. F. Z.

Brine spray refrigeration. S. C. BLOOM. *Am. Soc. Refrigerating Eng. J.* 8, 308-21(1922).—The successful operation of the spray systems depends upon the choice of a special nozzle of the non-clogging type. Diagrams of installations are furnished.

H. F. Z.

Some tests on welded ammonia containers. E. A. FRESSENDEN. *Am. Soc. Refrigerating Eng. J.* 8, 426-32(1922).—Vessels having forged welded seams are least reliable. This is due to incipient cracks occurring along the seams.

H. F. Z.

Some properties of hydrocarbon refrigerants. H. D. EDWARDS. *Am. Soc. Refrigerating Eng. J.* 8, 488-95(1922).—Hydrocarbon gasses are non-poisonous and non-corrosive. They are inflammable. A mixture of butane and propane furnishes a positive suction pressure. Standard fittings used in air service can be employed. Temps. 20° F. lower can be obtained with this mixt. of propane than with NH_3 . Other advantages and disadvantages are considered.

H. F. Z.

Refrigerating fluids. J. E. STARR. *Refrigerating Eng.* 9, 93-4(1922).—The advantages and disadvantages of NH_3 , SO_2 , CH_2Cl , $\text{C}_2\text{H}_5\text{Cl}$, CO_2 and N_2O as refrigerating fluids for large and small machines are discussed. Brief consideration is also given to CS_2 , Et_2O , CCl_4 and hydrocarbons.

H. F. Z.

Compound ammonia compression. G. A. HORNE. *Refrigerating Eng.* 9, 95-101(1922); cf. *Am. Soc. Refrigerating J.* 8, 245-308, 456-88(1922).—Test data obtained

from two installations, theory and practical applications of this type of refrigeration systems are considered. Open meeting discussions on the papers are included.

H. F. Z.

The plastometer as an instrument for process control. E. C. BINGHAM, H. D. BRUCH AND M. O. WOLBACH, JR. *J. Ind. Eng. Chem.* 14, 1014-5(1922).—Amorphous materials often lack definite characteristics, melting point, soly., and fluidity. The authors suggest the use of (1) the yield value, (2) the mobility, (3) the concn. of zero mobility—connected with the pore space, (4) the concn. of zero yield value—connected with particle size, and (5) the temp. at which the yield value becomes zero—analogue to the melting point. The authors also distinguish between plastic and pseudo-plastic materials.

EUGENE C. BINGHAM

Extinguishing generator fires with carbon dioxide. T. H. SORREN. *Elec. World* 80, 1089-91(1922); 6 illus.—Tests were made which indicate that air diluted with 10% CO₂ will not support combustion. Full details are given.

C. G. F.

Specifications for transmission oils. ANON. *J. Soc. Automotive Eng.* 11, 453 (1922).—The specifications prepd. by the Standards Committee of the Soc. of Autom. Engrs. covers the grades of petroleum oil suitable for the lubrication of transmission gears, differential gears, worm drives, and roller and ball bearings used with such motor vehicle equipment. Compounded lubricating oils contg. products other than those derived from petroleum are not covered by these specifications.

Specification no.	Grade.	Viscosity at		Pour test.	
		Flash point °F. Min.	210°F. Sec. min.	Saybolt °F. Max.	A. S. T. M. Method.
110	Winter	350	100	120	10
160	Summer	450	150	170	45

D. F. BROWN

The change in viscosity of oils with the temperature. W. H. HERSCHEL. *J. Ind. Eng. Chem.* 14, 715-23(1922).—Plotting logarithmic viscosities against logarithmic temps. gives linear curves which intersect at a point with lubricating oils of medium viscosity. Exceptions are found in spindle oils, air-plane motor oils, fatty, compounded, and unrefined oils.

EUGENE C. BINGHAM

Solid lubricants. ANON. *Dept. Sci. Ind. Res. Adv. Council Bull.* No. 4, 28 pp. (1920).—The characteristics of the following solid lubricants are described: natural and artificial graphite, talc, mica, sulfur, and white lead. Solid lubricants, particularly in colloidal condition, decrease wear in the starting of machinery or in bearings which are subjected to extraordinary pressure, in poorly lubricated or "oilless" bearings, in gears, in steam cylinders and valves, in metal cutting and wire drawing and on ropes and chains. In internal combustion engines, solid lubricants are of dubious advantage.

EUGENE C. BINGHAM

Technical examination of lubricating oil and grease. F. W. WATSON AND H. D. BELL. *J. Chem. Met. Soc. S. Africa* 22, 211-9(1922).—Various tests are described including the percentage of rosin, the volatility, and the softening point. In the *heat test* of a grease, a light grease should all run through a 200-mesh sieve between 190 and 210° F., and a heavy grease between 220° and 250° F. Light cup grease should contain 17-18% of lime soap with some 77% of mineral oil. Heavy cup grease contains 20-22% of lime soap with 74% of oil. Extra heavy cup grease contains 25% of lime soap and 70% of oil. Pitch and asphalt are not present in good cup greases but are legitimate in rope dressings. Data on commercial oils are given.

EUGENE C. BINGHAM

Some developments in insulating materials and processes in Great Britain. A. P. M. FLEMING. *India Rubber J.* 64, 641-4(1922).—Life tests of insulating materials under lab. conditions have heretofore given results not conforming well with results under practical service conditions over extensive periods. New procedures are sug-

gested in 2 directions: (1) the use of higher temp. limits whenever safe and (2) a comparison of machine performance on a basis of temp. rise in place of a basis of total temp. as recommended by the International Electrotech. Commission. Particulars are given of the facilities established for research, with a discussion of important developments in insulating materials and processes used in various types of elec. app., with special reference to thermal considerations. C. C. DAVIS

Determination of the electric strength of fibrous insulating materials. ANON. *Electrician* 89, 447(1922).—In the absence of recognized standard methods of carrying out elec. strength tests and in view of the many factors which may influence the result of these tests, a series of suggestions are offered for carrying out these tests based on a careful study by the Brit. Elec. and Allied Research Assoc. C. G. F.

Insulation failure—A pyroelectric effect. J. L. R. HAYDEN AND C. P. STEINMETZ. *Elec. World* 80, 885-8(1922).—Report of a detailed investigation of the mechanism of breakdown of solid insulation. Results show that the breakdown depends upon the relation between heat production and heat dissipation. Details are given. C. G. F.

Some features in condensing plant operation (HARDY) 1. Phenol-aldehyde condensation products (as elec. insulating material) (Brit. pat. 184,961) 18.

Purifying liquids. J. N. A. SAUER. Brit. 183,485, July 24, 1922. Sugar juices, H_2O , etc., are clarified by adding pptd. lime salts and then filtering. Ca carbonate, sulfite, sulfate, phosphate, oxalate and tartrates are mentioned as suitable salts. The process can be employed in combination with the known processes for softening H_2O by means of zeolites and other base-exchanging reagents. The pptn. may be effected at different temps., yielding different sizes of crystals, which are appropriate to different processes. Alkalies may be added to reduce the acidity of the liquid or produce any desired degree of alkalinity. Different salts may be used together or in succession. The residue from filtration may be purified by ignition or by treatment with HCl and re-used.

Purifying liquids. J. N. A. SAUER. Brit. 184,473, Aug. 9, 1922. Liquids such as sugar and glucose sirups and solns., mineral oils and greases, benzine, spirits, water, alc., and glycerol are purified by treatment with a ppt. of an insol. material formed outside the liquid and afterwards removed by filtration. The ppts. are especially effective in removing substances that have a chem. similarity to them, e. g., $Ca_3(PO_4)_2$ will remove Ca compds. and phosphates; $CaCO_3$ will remove Ca compds. and org. compds. The ppt. can be produced in any known way at a higher or lower temp. as a coarser or finer ppt. is required. The process may be used in combination with other known processes, e. g., sugar soln. may be treated with H_2SO_4 and then with $CaCO_3$, or decolorizing substances, such as decolorizing C or bleaching earth, may be employed along with the ppt. The ppt. is preferably used when freshly pptd., but it may be re-vivified after use and reused. When this is to be done the material treated is preferably first freed from coarse impurities by filtration, decantation, etc. The ppts. may be dissolved wholly or in part and repptd., or ignited or washed with a dil. acid or alkali, or these methods may be used in combination. The liquid may be treated with an elec. current during purification or catalysts or electrolytes added.

Cooling gases. SOC. L'AIR LIQUIDE (SOC. ANON. POUR L'ÉTUDE ET L'EXPLOITATION DES PROCÉDÉS G. CLAUDRÉ). Brit. 184,787, July 22, 1922. In the drying of air or gases by cooling in a heat-exchange app., rime formed on the walls of the tubes is detached by temporarily raising the temp. of the walls of the tubes, as by reversing the direction of flow of the air or gas to be cooled so that the incoming warm air, etc., first meets the parts of the tubes coated with rime. The detached rime falls by gravity, or is blown

hy the current of air, etc., to a chamber at the end of the tubes, where it is melted after normal working has been resumed and serves to cool the incoming air. The invention is applicable to the cooling of compressed air by N in air-liquefying processes. A suitable app. is specified.

Separating gaseous mixtures by liquefaction. SOC. L'AIR LIQUIDE (SOC. ANON. POUR L'ÉTUDE L'EXPLOITATION DES PROCÉDÉS G. CLAUDE). Brit. 184,454, July 22, 1922. In the sepn. of gaseous mixts., as air, by liquefaction and rectification, wherein there is removed from the rectifying column a mixt. contg. a considerable proportion of an element (A) of b. p. between those of the main constituents, a quantity of gas or liquid is returned to the rectifying column which is substantially equal in amt. to the mixt. removed and of the same compn. except for the absence of the element (A) of intermediate b. p. The mixt. withdrawn may be purified for the extn. of the A, etc., and the residual gases returned to the rectification column. A suitable app. is specified.

Recovering volatile solvents. MARTINI & HÜNEKE MASCHINENBAU AKT.-GESS. Brit. 184,483, Aug 10, 1922. In machines for coating webs of fabric with rubber, etc., in which a gas, preferably free from O, is circulated over the coated web and is cooled to sep. the volatile solvent, the casing of the app. is covered with heat-insulating material, and the condenser is located at a distance so that condensed solvent cannot drip back to the coated fabric. A suitable construction is specified. Cf. C. A. 16, 3720.

Concentrating and distilling liquids. C. H. CASPER. Brit. 184,760, Oct. 18, 1921. In concg. or distg. liquids such as fermented products, fruit juices, sugar soln., etc., a gaseous medium is maintained in continuous circulation over the liquid and through a condenser. A suitable construction is specified.

Heating and deaerating liquids. D. B. MORISON. Brit. 183,534, April 15, 1921. In the treatment described in 173,534, the deaeration effect is enhanced by recirculating liquid that has been treated and has had its temp. raised and from which the released air and gases have been definitely sepd., thereby mixing liquid of relatively high deaeration with liquid of lower temp. and lower deaeration, and subsequently submitting the mixt. to the heat treatment. A suitable app. is specified.

Heating liquids in storage tanks. B. MILLS, ELIZABETH and H. DAVIS. Brit. 184,198, Feb. 1, 1921. Viscous liquids in storage tanks are heated so as to render them more mobile by circulating, in the first instance, a certain amt. of a similar or the same liquid contained in a smaller tank by means of a pump through a coil surrounded by steam in a jacket by way of pipes. When this amt. is fluid, by adjustment of cocks a proportion of the hot fluid is introduced through pipes into any or all of the main storage tanks through shifting or rotary jets, the circulation being completed by the pipes. At a later stage distant parts of the tanks may be treated by introduction of hot fluid through other pipes and rotating nozzles. Fluid for use is taken from the tank which is kept warm when the installation is fully working by a small proportion of circulating liquid controlled by the cocks. A suitable construction is specified.

Separating materials of different specific gravity. J. A. FLETCHER. Brit. 184,049, July 26, 1921. App. for sepg. solids of different sp. gr. by means of an upward current of H₂O is provided with means for adjusting the flow of the liquid which carries away the lighter particles from the descending mixt. A suitable construction is specified.

Insulating compositions. A. A. SAMUEL. Brit. 184,164, July 12, 1922. Elec. and heat insulators are obtained by treating phenol-aldehyde condensation products with S or S chlorides.

Electric insulation. NAAMLIOOZE VENNOOTSCHAP PHILIPS' GLOEILAMPENFABRIEKEN. Brit. 184,436, Jan. 5, 1922. An insulating layer, especially applicable to condensers, is composed of a layer of a salt, e. g., CaF, with a max. thickness of 0.2×10^{-4} cm. per v. of disruptive voltage to which the layer is to be subjected. The layer is preferably prepd. by evapg. the salt in a high vacuum.

14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

Chemistry in relation to state water supplies. C. F. CATLETT. *J. Elisha Mitchell Sci. Soc.* 38, Nos. 1 & 2, 94-7(1922).—Brief discussion. H. W. E.

Relation of sea-water to ground water along coasts. J. S. BROWN. *Am. J. Science* 4, 274-94(1922); *Pub. Health Eng. Absts.* (Nov. 11, 1922).—The greatest distance from the shore at which shallow wells were contaminated by sea-water was 250 ft. When natural conditions are disturbed, as through a heavy drain on the ground water by pumping, the sea-water may be drawn great distances inland. Deep drilled wells are also subject to contamination, and should be located at least as far from the shore as the wells are deep. Expts. indicate fluctuations in salinity in water from wells can only rarely be correlated with the rise and fall of tides. Typographic and geologic conditions may largely det. the chances of well pollution by sea-water. G. C. BAKER

Ground water supplies from pre-glacial valleys. W. D. P. WAURE. *Munic. County Eng.* 62, 184-9(1922).—The geological features are discussed of two actual cases where subsurface supplies were obtained from a sand bed fed by a large area.

LANGDON PEARSE

Public water supplies in Illinois. H. F. FERGUSON. *Eng. Contr.* 57, 572-4; *J. Am. Water Works Assoc.* 9, 857-67(1922).—Statistics are given on water supplies with comment on improvements needed.

LANGDON PEARSE

Illinois Central improves its water supply in coal fields. C. R. KNOWLES. *Ry. Maintenance Eng.* 18, 300(1922).—Effects of summer droughts in southern Ill. coal fields have caused serious water shortage and serious pollution of surface supplies by acid drainage from mines. This has been largely overcome by installations of reservoirs. Plans and costs are given.

R. C. BARDWELL

Filtered well water recommended for Memphis, Tenn. FULLER AND MCCLINTOCK. *Eng. News-Record* 89, 566-7(1922).—Report compares cost of well water and Mississippi River supply. Conclusion: After the Fe and CO₂ are removed the well water supply is softer, cooler and produced cheaper than a filtered Miss. River supply. The Fe may be removed by aeration through nozzles, coke beds or addn. of CaO. Well supply contains 90 to 130 p. p. m. CO₂ and 0.2 to 0.6 p. p. m. Fe. It is proposed to sink 24 wells having a capacity of 1 million gal. per day each.

FRANK BACHMAN

Purification of the water supply of Avignon (France) by ozone. MARCEL PAILLET. *L'Ingenieur-Constructeur* (Sept.-Oct. 1921); *Le Genie Civil*, 597 (Dec. 31, 1921); *Bull. intern. office d'hyg. publ.* 14, 1125(1922).—Contaminated ground water is successfully treated by O₃ at an estd. net cost of 4 fr. per 1000 cu. m.

JACK J. HINMAN, JR.

Bradford (Eng.) water supply. LEWIS MITCHELL. *Can. Eng.* 42, 448(1922).—The supply is from impounding reservoirs, comparatively soft, and filtered through slow-sand filters. Daily consumption is 46 gal. (Imp.) per capita.

L. P.

Shooting water supply wells to increase their capacity. W. G. KIRCHOFFER. *Munic. County Eng.* 63, 172-4(1922).—The discharge of 20 to 30 lb. of high explosive in deep wells in rock has been found to increase the flow.

LANGDON PEARSE

Water supply from gravel strata. J. W. TOYNE. *Munic. County Eng.* 63, 21-2 (1922).—A log should be kept of every boring. The strainer mesh should be detd. from the sand. The casing should be sunk to the full depth, and pulled back after the strainer is placed.

LANGDON PEARSE

Cross connections, hypasses and emergency intakes on public water supplies. SOL PRINCUS. *J. Am. Water Works Assoc.* 9, 343-7(1922); *Eng. Contr.* 57, 452-3(1922).

LANGDON PEARSE

River intake difficulties. FULLER AND MCCLINTOCK. *Public Works* 53, 196-7

(1922).—The Mississippi River has a range of 46 ft. An intake structure would be 150 ft. high. The river bed shifts. An intake pier or tunnel would cost \$1,000,000 or more; hence continued used of artesian well supply was advised. L. P.

Statistical record of Toronto water, 1912-22. N. J. HOWARD. *Can. Eng.* 42, 469-76(1922).

LANGDON PEARSE

Underground hygiene and sanitation. R. R. SAYERS AND P. A. SURGEON. *Bur. Mines, Repts. of Investigations* No. 2391, 11 pp.(1922).—Piping of drinking water underground is the safest method of distribution; if containers such as barrels are used for taking the water underground they should be tightly closed and fitted only with a faucet or drinking fountain for withdrawing the water. Such containers should be washed thoroughly and sterilized at frequent intervals. Water carrier systems are not practical for sewage disposal in most mines. Water and animal-tight removable containers for closets with provision for disinfection are advised. For further prevention of disease good ventilation, wet drilling and wet mining methods are recommended.

G. C. B.

Financial gain from improving old water systems. L. W. COX. *Munic. County Eng.* 62, 62-3(1922).—Data are given on a no. of Iowa towns on consumption and source of supply. Figures are given to show the benefit by increased use if water is purified.

LANGDON PEARSE

New method of purifying water. H. W. CLARK. *J. New Eng. Water Works Assoc.* 36, 385-91; *Public Works* 53, 197-8(1922).—To make a sparkling water of low color of soft waters, C. suggests loading sand of a slow sand filter with coagulant and operating at a rate of 5 to 6 million gal. per day per acre. With $Al_2(SO_4)_3$ from 75 to 225 tons per acre have been used. $Al(OH)_3$ is pptd. by alternating doses of solns. of soda ash and alum. To remove coloring matter, held in the filter, a weak soln. of NaOH is applied every 2 or 3 months. From 66 to 78% of color is removed. The wash water runs from 2.5 to 5.5%. L. P.

Treatment of hard impure waters with alum. WILLIAM CORR. *Eng. Contr.* 58, 134-5; *Can. Eng.* 42, 519-21(1922).—In the treatment of water with $Al_2(SO_4)_3$, an increase of bicarbonates or org. matter requires more coagulant. The optimum amt. of $Al_2(SO_4)_3$ increases with the alky. of the water. The p_H is a measure of the amt. of coagulant required. The proper amt. can only be detd. by expt. L. P.

Estimation of chloride hardness in water. H. BECKURTS. *Z. angew. Chem.* 35, 434-5(1922).—A general discussion is given of the detn. of $MgCl_2$ in water. The detn. of Mg is very bothersome so that of Cl is favored. Disadvantages encountered are: conversion of other Mg salts into $MgCl_2$, by other chlorides; $MgCl_2$ may not be removed if an alc. extn. is used, or $CaCl_2$, $Mg(NO_3)_2$, and other salts may be extd. and interfere. The method of Boshardt and Burawzow, as used by Tricke, was the most satisfactory. 500 cc. of water were evapd. to dryness, the residue was extd. with alc.-ether soln., equal parts by vol., and the Cl detd. by titration of the ext., or a gravimetric analysis of Ca and Mg in the total mass. This method showed that: about 99% of the $MgCl_2$ was recovered; the presence of NaCl gave a rather const. value corresponding to 5.4 mg. per l. or 0.43° hardness (it is recommended that this value be deducted as a correction); nitrates as ordinarily found in water do not interfere; the presence of NH_4Cl may disturb the results.

H. D. CARTER

Combination of the lime soda and zeolite water softening process. L. M. BORTH. *Munic. County Eng.* 62, 220-1(1922).—B. advocates a residual hardness of less than 85 p. p. m. and even below 50.

LANGDON PEARSE

Recent advances in the bacteriological examination of water. W. J. WILSON. *J. State Med.* 30, 437-43(1922); *Pub. Health Eng. Absts.* (Nov. 11, 1922).—In addn. to the quant. detn. of *B. coli*, W. recommends the typing of bacilli by means of the methyl red, Voges-Proskauer and Koser's uric acid tests.

G. C. BAKER

The *Bacillus coli* tests. M. F. STEIN. *Eng. Contr.* 57, 445-6(1922).—The relation between positive results in samples of 1 and 10 cc. is discussed mathematically.

LANGDON PEARSE

Water-borne typhoid in Havre. J. SANARENS. *Public Works* 52, 441-2(1922).—Surface pollution quickly reaches the water supply drawn from chalk. Typhoid follows rains.

LANGDON PEARSE

Copper sulfate treatment for preventing algae growths in lakes and reservoirs. N. L. HUFF. *Munic. Survey & Eng. Soc. Can. Eng.* 43, 298-301; *Eng. Contr.* 58, 33-6(1922).—H. describes algae types, and details limiting safe doses of CuSO_4 for various fish. Dose to destroy several common algae may injure trout. Treatment of various lakes are covered. Competent supervision is urged.

LANGDON PEARSE

Observations on chlorination tastes and odor. W. DONALDSON. *Eng. Contr.* 58, 74-7; *Can. Eng.* 43, 328-7; *J. Am. Water Works Assoc.* 9, 885-91(1922).

LANGDON PEARSE

Prevention of tastes and odors due to microscopic organisms. W. W. BRUSH. *Eng. Contr.* 57, 560-1; *Can. Eng.* 42, 673-4(1922).

LANGDON PEARSE

Stream pollution investigation. S. A. FORBES, F. O. JORDAN AND LANGDON PEARSE. *Eng. Contr.* 58, 251; *Public Works* 53, 172-3(1922).—This is a memorandum to the Surgeon General, U. S. Public Health Service, on the powers of the service, present tendency regarding stream pollution, its regulation, and suggestions for future studies.

LANGDON PEARSE

Quantitative data in stream pollution investigations. E. B. PHELPS. *Munic. County Eng.* 63, 22-4(1922); cf. *C. A.* 16, 1121.—Stream pollution should be studied from the standpoint of wastes whether injurious in themselves, or by decompon. The biochem. O demand is a most helpful indicator and may be applied to stream pollution problems most successfully.

LANGDON PEARSE

Stream pollution investigation. J. K. HOSKINS. *Pub. Works* 53, 172-3; *Eng. Contr.* 57, 449-52; *Can. Eng.* 43, 232(1922).—H. details the work of U. S. Public Health Service to det. laws. of self-purification of streams, covering methods of hydro-metric studies, sanitary surveys and analyses both biological, chem. and bacteriol. The future work of the U. S. P. H. S. is mentioned.

LANGDON PEARSE

Reducing the industrial pollution of Indiana streams. R. LIEBER. *Munic. County Eng.* 63, 148(1922).—Steps are being taken to reduce pollution of streams by industrial wastes.

LANGDON PEARSE

Experience with algae at Davenport. C. R. HENDERSON. *J. Am. Water Works Assoc.*, July 1922; *Eng. Contr.* 58, 123(1922).—The use of Cl seemed helpful when the filters at Davenport were bothered by algae. In an open reservoir CuSO_4 proved the best treatment.

LANGDON PEARSE

The W. & T. vacuum feed chlorinator. ANON. *Munic. County Eng.* 63, 27-8 (1922).—This describes the Wallace and Tiernan vacuum feed chlorinator.

LANGDON PEARSE

A survey of bleaching powder tubes for use with the Lyster bag. C. B. WOOD. *Military Surgeon* 51, 444-50(1922); *Pub. Health Eng. Absts.* (Nov. 19, 1922). As a result of a large no. of phys. and chem. tests the following conclusions were made: (1) improved methods of packing would decrease breakage; (2) good tubes, with dry content, 2 yrs. old, will give to 36 gals. (a Lyster bag full) of water a little over 1 p. m. free Cl; (3) in perfect tubes CaOCl_2 deteriorates at a rate of about 0.5% monthly; (4) deterioration is more rapid in warmer climates; (5) survey of stocks at regular intervals, dated from the date of manuf., is desirable.

G. C. BAKER

Air and relief valves. M. M. BORDEN. *Can. Eng.* 43, 174-6(1922).

LANGDON PEARSE

St. Louis water works operation. *Ann. Rept.* 1921-22; *Public Works* 53, 102-6(1922).—Encouraging expts. have indicated the feasibility of burning pulverized coal. Buying coal in a B. t. u. value and percentage of ash guarantee has proved worth while. A new pumping plant is being designed to handle 200 mil. gal. per 24 hr. using 1,000 b. p. boiler units and steam between 250 and 300 lb. pressure, with 150° to 200° superheat. A new intake is proposed to care for fluctuation of 34 ft. In 7 yrs. filter sand has become coated to amount to 10% by wt. Settling basins and conduits have been cleaned. For conduits a cable drawn barrow has been very useful. LANGDON PEARSE

Water treatment works of Buenos Aires, Argentine Republic. M. L. NEGRI AND H. W. WANDR. *Eng. News-Record* 89, 602-3(1922).—The water supply is obtained from the Rio de la Plate river. It is pumped to coagulation and sedimentation basins where alum is added, followed by filtration through 10 slow sand filters with a total area of 13.3 acres. The coagulation and sedimentation basins remove 80 to 90% of the bacteria. No results on filter efficiency are given. F. B.

Cleaning a mixing conduit of lime deposits. C. M. DAILY. *Eng. News-Record* 89, 695(1922).—After a few months service the mixing conduit at St. Louis waterworks had 2 ft. of soft mud on the bottom and a small amt. of lime scale on the sides. The deposits were removed by means of a disc harrowed through the conduit. F. B.

New water purification and pumping plant at Pryor Creek, Oklahoma. L. M. BUSH. *Munic. County Eng.* 62, 61-2(1922).—The plant supplies 300,000 gal. per 24 hr. and is electrically driven. The low lift pumps raise the water to settling basins, with dry alum feed, the high lift pumps discharging through pressure filters. L. P.

Filter plant operation at St. Louis. E. E. WALL. *Ann. Rept. Water Comm'r.* 1922; *Eng. Contr.* 58, 250(1922).—Cost of filtration was \$4.44 per mil. gal. The rate of filtration ran from 74.35 to 98.31 mil. gal. per acre per 24 hr. Runs were from 11.16 to 237.58 hr., averaging 70.98 hrs. Wash water rate was changed from 15.7 to 15.0 gal. per ft.² per min. The softening at the plant saves the city \$920 per day in soap. LANGDON PEARSE

Water purification plant operation in Illinois. M. W. COWLES. *Eng. Contr.* 57, 569-72(1922).—This is a complete discussion of treatment preliminary to filtration, use of coagulating chemicals, mixing raw water with coagulants, no. of plants, control, size of sand, type of wash, underdrain system, and sterilization. L. P.

Pumping and filter plant at Sturgeon Falls, Ont. ANON. *Can. Eng.* 42, 599-60(1922). LANGDON PEARSE

Laboratory control at Illinois water purification plant. M. W. COWLES. *Eng. Contr.* 58, 256(1922).—Control may be by periodic analyses or by local control. The latter is preferred. Monthly reports are desired. LANGDON PEARSE

Special features of recent filter plant design. PAUL HANSEN. *Eng. Contr.* 57, 438-40(1922).—In the design of small plants economy of construction and operation has been sought. One man operation, compact pipe galleries, lighting, chem. control and valve operation are all valuable. LANGDON PEARSE

Modern water filtration plant at Ashland, Ky. D. H. MAXWELL. *Munic. County Eng.* 63, 127-30(1922).—The plant serves 15,000 people with a rated capacity of 2.67 mil. gal. per 24 hr. Work was done on a cost plus sliding fee basis. Two intakes are provided at different levels. The plant includes low lift pumps (2 motor driven, 1 gasoline engine driven) coagulating basins, high service pumps and filters. L. P.

Observations on the operation of rapid sand filters. J. W. ELLMS. *Can. Eng.* 43, 330(1922).—After discussing the general problem, E. suggests room for research. LANGDON PEARSE

Extensive boiler-water treating on C. M. & St. P. Ry. C. H. KOYL. *Eng. News-Record* 89, 560-2; *Ry. Age* 73, 573; *Ry. Maintenance Eng.* 18, 344(1922).—Operating

conditions on the C. M. & St. P. Ry. were much improved by the installation of water-softening plants. A typical plant consists of soln., mixing and sedimentation tanks. Lime, soda ash and FeSO_4 are added. Thorough mixing for 25 to 50 min. is essential for complete pptn. These plants have a capacity of 15,000 gal. per hr. Sludge is removed by opening valves for 30 sec. controlling a system of perforated sludge pipes lying on the bottom of the settling tank.

FRANK BACHMANN

A lime, soda ash chart. F. D. YEATON. *Ry. Maintenance Eng.* 13, No. 5, 169 (1922).—Chart gives lbs. Na_2CO_3 and $\text{Ca}(\text{OH})_2$ per 1000 gal. water for varying amts. of incrusting salts shown as gr. per gal.

R. C. BARDWELL

Electrolytic or direct oxidation and the Lima deadlock. GEO. W. FULLER. *Eng. News-Record* 89, 658-9 (1922).—Both the trickling filter system and direct-oxidation process are being considered at Lima, O. The comparative costs of the two processes are: \$691,000 for the trickling filter and \$400,000 for the direct-oxidation process. Annual operating cost of the former is estd. at \$15,000 as against \$40,000 for the latter.

FRANK BACHMANN

Layer of fine sand within slow sand filter at Chester, England. F. STORR AND C. W. BENNETT. *Eng. News-Record* 89, 603 (1922); cf. *C. A.* 16, 2748.—By means of a layer of fine sand 15' from the top of the filter, greater removal of bacteria is claimed. The rate of filtration is 940,000 to 2,500,000 gal. per day.

F. B.

A new method of rating water-bearing sands and gravel. W. G. KIRCHOFFER. *Public Works* 53, 64-6 (1922).—Method suggested is based on fineness modulus of Abrams for concrete sands. Analytical data are given.

LANGDON PHARSH

Application of copper sulfate to reservoirs. J. E. GARRATT. *Can. Eng.* 43, 396-7 (1922).— CuSO_4 was applied in a large reservoir contg. 1,800 mil. gal. by towing 2 bags of CuSO_4 behind a motor boat running 6 mi. per hr. 100 lb. dissolved in 5 min. Applications of 1.5 to 2.5 lb. per mil. gal. were made monthly.

L. P.

The treatment of sewage and industrial wastes. F. W. MOHLMAN. *Chem. Bull.* (Chicago) 9, 250-3 (1922).—The work of the Sanitary District of Chicago is outlined. The Maywood activated sludge plant which will treat the sewage of more than 40,000 people comprises a grit-chamber and fine screen before aeration. The activated sludge part of the plant is in 4 units, each having different conditions of depth, flow, aeration and sedimentation. Presses, driers and a centrifuge are part of the equipment. The Calumet sewage treatment plant includes 30 Imhoff tanks and 2 additional tanks with aerators and settling tanks for activated sludge treatment, and will treat the sewage of 150,000 people. A small sprinkling filter has also been constructed. A filter, centrifuge and drier together with a lab. are provided. A superactivated sludge plant is being designed for treating the sewage of 800,000 people on the North Side. A very small treatment plant at Morton Grove, consisting of Imhoff tanks and sprinkling filters, has been in operation for several years. Four testing stations have been operated, one treating domestic sewage, one treating packing-house waste, one chrome tannery wastes and the 4th, still in operation at Argo, treating corn products waste. Industrial wastes are more coned. than domestic sewage and have required more air and more careful attention, while tannery wastes were toxic if too much lime was present—corn products waste has only been purified when mixed with 3 vols. of condenser water; gluten and starch wastes will not form and maintain the proper kind of sludge. De-watering expts. with a small suction filter (American) has proved encouraging; adjusting the pH has proved helpful but biologic conditions in the aerating tanks seem of greater importance. Various forms of aeration have been tried. Analyses of different sludges are given and the field and lab. work is outlined.

G. C. BAKER

Developments in sewage disposal. C. J. MACKENZIE. *Can. Eng.* 43, 256-9 (1922).—M. reviews history of sand filters, contact beds, trickling filters, sedimentation, septic tank, Imhoff tank, activated sludge and Miles acid process.

L. P.

Sewage treatment. R. O. W. RONGERS. *Can. Eng.* 43, 321-3(1922).—In a report on sewerage for York Township, the treatment problem is reviewed. L. P.

Purification of sewage and treatment of domestic wastes. (Annual Review.) ROLANTS. *Rev. hyg.* 44, 731-41(1922).—A review of progress in 1921 in England, France and America. Emphasis is on the English work. JACK J. HINMAN, JR.

The sewage treatment problem in the U. S. from the standpoint of sludge. LANGDON PEARSE, *et al.* *Eng. Contr.* 58, 83-90(1922).—This is a statistical review of conditions in cities from 25,000 population up on treatment works and sludge. Some use of sludge by farmers is shown and in a few cases price of \$2.00 per cu. yd. was reported from sales. Sludge analyses are given: N content on dry basis, Imhoff 2.23, secondary tanks of sprinkling filters 3.02, chem. pptn. 1.62, activated sludge (domestic) 5.23%.

LANGDON PEARSE

Some recent experiences in the process of sewage disposal. J. W. H. JOHNSON. *Can. Eng.* 43, 367-8(1922).—The activated sludge process works well in liquids slightly alk., but not in acid or very alk. solns. Only 1% of air blown is absorbed. Biological oxidation is different from chem.

LANGDON PEARSE

Some aspects of the sewage purification problem. F. W. HARRIS. *Can. Eng.* 43, 494-5(1922).—H. details experience at Dalmarnock with *Achorides viaticus* inoculation of sprinkling filters successfully to relieve ponding. At Glasgow activated sludge expts. have been made with surface agitation, by paddles in a tank 5 ft. deep with channels 3 ft. 6 in. wide, and 640 ft. long.

LANGDON PEARSE

Industrial effluent disposal. ANON. *Can. Eng.* 43, 395(1922).—Effluents from by-products gas works have given offense. They may be treated by passing liquor down a scrubber tower, in which steam rises upwards. One cu. ft. of scrubber packing is required per 240 gal. liquor.

L. P.

The disposal of sewage screenings. WM. F. MORSE. *Munic. County Eng.* 62, 200-1(1922).—The incineration of screenings is cleanly and practicable, even though they have little calorific value.

L. P.

Some data on the bio-aeration of sewage. H. N. STAFFORD AND A. W. WARD. *J. Roy. Army Med. Corps* 39 (July, 1922); *J. Tropical Med.* 25, 301(Sept. 15, 1922).—A description and diagram of the Blackpool plant, modeled after Sheffield, is given, together with analytical data. In a bio-aeration plant working to standards of chem. efficiency there is marked reduction of organisms, particularly coli forms, but the reduction is no better than in other recognized forms of sewage treatment. The reduction of *B. typhosus* is much more marked. Coli-form organisms are not mere intruders, but probably play a part in the purification. Sterilization of effluent may be effected by 4 p. p. m. Cl.

JACK J. HINMAN, JR.

Aeration experiments at Bury. JOSHUA BOLTON. *Eng. Contr.* 57, 527; *Surveyor* 61, 417, 435; *Can. Eng.* 43, 282-3(1922).—B. quotes from sewage treatment and disposal by T. Wardle to show that the idea of activated sludge may have been conceived 28 years ago. In expts. at Bury settled liquid is treated by a mech. agitator revolving at the center of a circular tank, throwing the sewage out. A central cylinder haffle promotes circulation. Power used is 15 h. p. per mil. gal. No nitrates are produced.

LANGDON PEARSE

Present status of the activated sludge process of sewage treatment. LANGDON PEARSE. *Munic. County Eng.* 63, 184-9(1922).—This is a brief review of the activated sludge situation with data on tests made in U. S., estimates of cost, and analyses of sludge and sewage.

LANGDON PEARSE

Prevention of sewage contamination in Ontario. F. A. DALLYN. *Can. Eng.* 42, 522-4, 601-2(1922).—The Ontario Provincial Board of Health is actively endeavoring to protect water supplies. Branch labs. have been established.

L. P.

Experiments on the bacterial purification of sewage by the activated sludge process. PAUL COURMONT AND A. ROCHAIX. *Rev. hyg.* 44, 907-19(1922).—Irregular results were obtained in the reduction of bacteria when using the activated sludge process, max. removal being about 50%. Removal of *B. coli* likewise was irregular with a max. reduction of 80%. Aeration without activated sludge gave 95% reduction of *B. coli*. Aeration of activated sludge carried to the point of removal of NH_3 (two weeks) completely removes *B. coli*; six hrs. aeration seems to destroy cholera vibrios, but to have slight effect on *B. typhosus* and the paratyphoid bacilli. In sewage to which activated sludge is added, whether aerated or not, the typhoid and paratyphoid organisms die in 24 hrs. to 3 days. Bibliography of 24 titles is given. JACK J. HINMAN, JR.

Rhythm of the disappearance of ammonia during the purification of sewage by activated sludge. PAUL COURMONT, A. ROCHAIX, AND F. LAUPIN. *Compt. rend.* 173, 1498-9(1921); *J. Soc. Chem. Ind.* 41, 116A.—Further exptl. evidence is given in support of the view that the disappearance of NH_3 is a linear function of the time. JACK J. HINMAN, JR.

Amount and rhythm of disappearance of organic matter during purification of sewage by the activated sludge process. PAUL COURMONT, A. ROCHAIX AND F. LAUPIN. *Compt. rend.* 173, 1199-1201(1921); *J. Soc. Chem. Ind.* 41, 77A.—In 12 cases the amt. of org. matter in the effluent before the addition of activated sludge was 61-68% of that in crude sewage. After adding the activated sludge the org. matter decreased suddenly on mixing, and afterwards decreased at a slower rate during aeration. After 2½ hrs. aeration the org. matter was about 50% of that before aeration. J. J. H., JR.

Notes of two new sewage treatment processes. L. L. TRIBUS. *Munic. County Eng.* 63, 120-2(1922).—T. discusses the MacLachlan process using SO_2 gas and the Selo process, a lime electrolytic process in which the sludge is treated with salt and electrolyzed with air agitation. Sludge dries readily. LANGDON PEARSE

Miles acid process of sewage treatment. F. W. MOHLMAN. *Can. Eng.* 43, 477; *Public Works* 52, 400-2(1922). See C. A. 16, 1826. LANGDON PEARSE

Operation of sewage treatment works. BURNS AND McDONNELL. *Eng. Contr.* 58, 249; *Public Works* 53, 92-3(1922).—General suggestions are given in operating details. LANGDON PEARSE

Small industrial sewage treatment plant. G. L. ROBINSON. *Munic. County Eng.* 63, 29-30(1922).—The sewage of a factory employing 420 people is to be settled and sterilized by $\text{Ca}(\text{OCl})_2$. LANGDON PEARSE

One years operation of direct oxidation sewage-works at Allentown. H. F. BASCOM. *Eng. News-Record* 89, 659-60; *Munic. County Eng.* 63, 165-71(1922).—Max. capacity of the plant is 2.8 million gal. per day. The plant includes fine screens ¼" circular perforations, grit chambers, lime dosing app., 3 sets of 1 million gal. per day electrolyzers, sedimentation basins with a detention of 1½ to 2 hrs., and sludge drying beds. Removals obtained were: suspended solids 54, O consumed 53, N 39, bacteria at 37° 99.6, and *B. coli* 99.98%. Sludge as removed from the sedimentation basin contained 94% moisture and amounts to 21 cu. yd. per million gal. Cost of treatment is estd. at \$20.30 per million gal. FRANK BACHMANN

Sewage pumping station for London, Ont. H. S. PHILLIPS. *Can. Eng.* 43, 447-9(1922).—The pumping station is octagonal. Four 8-inch horizontal centrifugals are float operated. LANGDON PEARSE

Features of sewage disposal plant at Randolph, Nebraska. K. C. GAYNOR. *Munic. County Eng.* 62, 170-2(1922).—The sewage of 1,200 people is pumped into an Imhoff tank, thence to a sprinkling filter. LANGDON PEARSE

Water supply in its relation to sewage disposal. J. C. KRITT. *Can. Eng.* 42, 608(1922).—K. discusses local the situation along the Detroit River for Essex County.

Sewage is carried below intakes of Windsor and Walkerville. Water filtration is needed however.

LANGDON PEARSE

Methods and cost of mechanical cleaning filtering media of sewage beds. J. H. ANNOTT. *Eng. Contr.* 58, 208-9(1922).—A. describes types of washers, one having flat tables or jiggling trays with water, the other having revolving cylinders. Methods of handling are described.

LANGDON PEARSE

Storm water run-off in cities. CRAS. B. BURDICK. *Proc. Iowa Eng. Soc.* 37, 44 (1922).—Calcs. of run-off for design of sewer systems have been empirically handled. Thus calcs. for Baltimore are about 10 times those for Gary. A hitherto unpublished table summarizing data on storms which had a rate at least equal to 0.74 in. per hr. is prep'd. for 23 cities of U. S. east of Mississippi from data of the U. S. Housing Commission, 1918.

JACK J. HINMAN, JR.

Design of sewage dosing tanks for trickling filters. E. B. BESSERLIVRE. *Eng. News-Record* 89, 552-4(1922).

FRANK BACHMANN

The largest sewage sprinkler in the world. ANON. *Munic. Eng. Sanit. Record* (April 20, 1922); *Eng. Contr.* 57, 527(1922).—This is a rotary sprinkler serving a circle 180 ft. diam.

LANGDON PEARSE

Comments on Imhoff tanks. W. G. KIRCHOFFER. *Public Works* 52, 318(1922).

LANGDON PEARSE

Imhoff tank results. J. R. DOWNES. *Public Works* 52, 304-5(1922).—A detailed discussion of pro and con of tank results from operating standpoint.

L. P.

Sludge digestion at Birmingham. L. H. SALTER. *Public Works* 53, 107-10 (1922).—At Birmingham, Ala., 150,000 are served by sewers, 50,000 by box and can privy system. There are 2 main treatment plants, one contg. septic tanks and contact beds, the other sedimentation tanks, sludge digestion tanks and contact beds. Slag has not proved satisfactory in contact beds, disintegrating somewhat after 6 yrs. and packing. Sludge is pumped into sludge digestion tanks every 2 or 3 days, and is retained for 14 to 21 days, until working ceases. It is then air dried for 15 to 30 days. N content is 2.23%.

LANGDON PEARSE

Disposal of activated sludge. R. H. EAGLES. *Public Works* 53, 111-2; *Can. Eng.* 43, 450-60(1922).—The use of SO₂ gas has been tested at Houston, Indianapolis, and Gastonia, and appears to produce an ionic condition favorable to dewatering, preventing decompn. and increasing the NH₃ content. Seventy-five lbs. crude S per mil gal. sewage is used.

LANGDON PEARSE

Dewatering sludge. J. D. WATSON. *Can. Eng.* 43, 350-1(1922).—W. describes sep. sludge digestion methods at Birmingham, England, whereby ripe sludge is added to fresh. Steam is used in cold weather to heat the sludge. Storage of 4 months is sufficient, but more is advisable. Humus from sprinkling filters is hard to handle.

LANGDON PEARSE

Disposal of packing house waste by activated sludge at Mason City, Iowa. EDWARD BARTOW. *Proc. Iowa Eng. Soc.* 34, 51(1922).—B. gives a description of a plant installed for the packing house of Jacob E. Decker and Sons of Mason City, Iowa. Waste is much more concd. than ordinary sewage.

JACK J. HINMAN, JR.

Activated sludge. EDWARD BARTOW and G. C. BAKER. *J. Ind. Eng. Chem.* 14, 842-3(1922); cf. *C. A.* 15, 1957.—The article is a review of the installations of activated sludge plants and recent developments in the process. Continuous air diffusion method is usually preferred, but some aeration may be dispensed with, provided some other form is used. It has been possible to reduce the moisture content of the sludge to 72-5% by filter-pressing or centrifuging. SO₂ used in a dewatering process reduced the moisture to 74%. The dried sludge, with a N content of from 4 to 7%, makes a good fertilizer. New development is irrigation and fertilization with wet activated sludge distributed by means of mains and service pipes.

H. D. CARTER

Activated sludge plant at Brampton, Ont. W. M. TREADGOLD. *Can. Eng. 42*, 459-61 (1922).—Existing sedimentation tanks were reconstructed to serve as aeration units. A new settling tank with hopper bottom was built. The plant handles about 250,000 gal. per 24 hr. Two cu. yd. sludge per day are put on drying beds (2 each 20×80 ft.).

LANGDON PEARSE

Fertilizing value of activated sludge. H. D. BROWN. *39th Ann. Rept. Bd. Health Ontario; Can. Eng. 42*, 440-1 (1922).—The air-dried sludge contained 4.5% N and 14% H_2O . Field expts. were made on $\frac{1}{2}$ acre. The amts. of sludge used varied, being 40, 80 and 120 lbs. N per acre.

LANGDON PEARSE

Application of liquid sludge to farm land. ROBERT EATON. *Eng. Contr. 58*, 207 (1922).

LANGDON PEARSE

Sanitary districts. SYMPOSIUM. *Proc. Ill. Soc. Eng. 37*, 32 (1922).—Papers by Paul Hansen, Harry F. Ferguson, and W. C. Field on experience with sanitary districts in Illinois.

JACK J. HINMAN, JR.

Sanitating a small city. W. A. HARDENBERGH. *Public Works 53*, 148-50 (1922).—H. details the Alabama health law and describes the use of standard septic tanks (270 gal. and 700 gal. for not more than 10 and 25 people, resp.).

LANGDON PEARSE

Sterilization of swimming pool supplies. J. VON BENSCHOTEN. *Can. Eng. 42*, 477 (1922).—Recirculating system is recommended in preference to fill and draw system, with liquid Cl sterilization.

LANGDON PEARSE

Odor elimination, New Bedford garbage plant. W. J. SPRINGBORN. *Public Works 52*, 442-3 (1922).—The use of Cl gas eliminates org. odors. With 7 sec. contact 900 lb. liquid Cl deodorized vapors from 4098 tons of garbage.

LANGDON PEARSE

Egyptian ophthalmia (trachoma) and public swimming pools. ANON. *Gesundh. Ing. 260* (May 20, 1922); *Bull. Office Intern. Hyg. Pub. 14*, 973 (Aug. 1922).—Granular conjunctivitis was observed in young men who frequented swimming pools at Cologne, Berlin and Neukölln. At the latter place the installation of liquid Cl app. has given good results and it is proposed to install an app. at a pool at Friedrichsbain.

JACK J. HINMAN, JR.

Apparatus for adding reagents to liquids (Brit. pat. 183,357) 1.

Softening water; removing scale from boilers. U. G. ALLENDAR. Brit. 185,365, Jan. 17, 1922. A fluid for softening H_2O and removing scale from boilers, etc., consists of gambier, caustic soda, soda crystals, borax, alum, NH_4Cl , and water.

Preventing and removing incrustation. ZYNKARA CO., LTD. and W. A. CROSS. Brit. 185,035, Oct. 7, 1921. A solid compn. for preventing corrosion and removing incrustation in boilers, etc., comprizes an alk. compd., finely divided Zn or other metal electropositive to the metal of which the boiler is made, and a substance of comparatively low m. p. and unattacked by caustic alkali, such as paraffin wax, to protect the alk. material from the atm. Suitable proportions are, by wt., $NaOH$ 11, Zn 7, and paraffin wax 4 parts. The materials are mixed in a fluid state and cast in molds and the blocks may be afterwards coated with wax.

Boiler compounds; cattle food. J. W. RIGBY. Brit. 183,371, Aug. 17, 1921. Pulped peas and linseed are boiled in H_2O , Na_2CO_3 is added and the mixt. again boiled. The liquid is decanted and the residue is boiled with an equal quantity of H_2O . The resulting liquid is decanted and added to the previously decanted liquid. The residue may be dried and used for making cattle food.

Purification of sewage. W. JONES. Can. 224,888, Oct. 17, 1922. A tank open to the atm. has at its upper part overhanging portions which bend and direct the liquid stream from the vertical to the horizontal direction and means for supplying air to the liquid by which it is circulated transversely in the tank.

Cooling and purifying air in buildings. C. L. BURDICK. *Brit.* 184,583, May 18, 1921. Valves for regulating the admission of gas or liquid or both to a spraying device are controlled by an electromagnetic device in order to operate the sprays automatically at predetd. intervals. As a spraying medium, O or compressed air enriched with O or ozone may be employed.

15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

Classification of soils. F. J. ALWAY. *Proc. Minn. Surveyors and Engrs. Soc.* 26 and 27, 62(1921-22).—A general paper on the character of soils as applied to land drainage. Classification is based on moisture equiv. equal to the no. of lbs. of water retained by 100 lbs. soil after centrifuging. There are about 7 million acres of peat soils in Minn.

JACK J. HINMAN, JR.

Biochemical methods for the determination of the fertility of the soil. JULIUS STOKLASA. *Chem.-Ztg.* 46, 681-3(1922).—The factors affecting the fertility of soils are: (1) its air and H_2O capacity; (2) no. of active microorganisms present; (3) quantity and chem. compn. of org. substances; (4) availability of the org. substances; (5) chem. reaction of the soil; (6) mech. condition of the soil; (7) kind of fertilizers used; and (8) kind of crops grown. The air and H_2O capacity of the soil are of prime importance for they govern, to a large extent, the growth of bacteria, fungi, algae, protozoa and other forms of life. Bacterial counts, as a rule, give a good indication of the fertility of a soil. The total no. of microorganisms present depend upon the kind of crop previously grown. S. states that in the first 25 cm. of soil the no. of microorganisms averaged 33 million per g. of dry soil for oat fields and 100 million for alfalfa fields. Other cropped soils lay in the following order, rye, potatoes, barley, sugar beets, and clover. The total no. of bacteria are, in general, affected by the H-ion concn. of the soil. Heavy concns. of org. substances and insufficient O supply promote the development of anaerobic bacteria. When the air capacity of a soil falls below 2% anaerobic organisms predominate. On the basis of their ability to utilize different forms of N and C, S. divides soil bacteria into 3 classes: (1) those that require neither org. C nor org. N; (2) those that require org. C but not org. N and (3) those that require both org. C and org. N. The detn. of the respiration intensity of the microorganisms in the soil serves as an excellent indication of relative fertility since it was found that a certain relation exists between the quantity of CO_2 produced and the total no. of microorganisms and the available org. matter present. For the detn. of the quantity of CO_2 produced, S. used the following method: To 1 kg. of air-dried soil, taken to a depth of 25 cm., is added 25% H_2O . The sample is incubated at 20° for 24 hrs. and the quantity of CO_2 evolved detd. From 1 kg. of an infertile dry soil, poor in org. matter, 8-14 mg. CO_2 were produced, while from a good beet soil the evolution of CO_2 was 56-68 mg. It is estd. that 150 kg. CO_2 are evolved from a hectare of moderately good, cultivated soil every 24 hrs. at a temp. of 15° . Soils contg. relatively high amts. of radioactive elements yield better crops than those poor in such elements.

K. D. JACOB

Sulfur oxidation in "black-alkali" soils. W. RUDOLFS. *Soil Science* 13, 215-29 (1922).—The effects of applications of S of from 100 to 3500 lbs. per acre upon the reaction and phys. condition of some alkali soils from California are reported. Soils with an original p_H as high as 9.3 were reduced to neutrality by the heavier applications of S after 8-12 wks. incubation. Practically all of the S had been oxidized to SO_4 after 18 wks. No close correlation was noted between the p_H values and the amts. of S oxidized. Carbonates were transformed into bicarbonates with increase in S oxidation. SO_4 formation was correlated with flocculation and decreasing apparent sp.

gr. The biological flora, expressed in no. of colonies on agar plates, varied directly with the change in p_H . Molds and actinomycetes predominated in the untreated alk. soils while relatively few were found on the soils brought to the neutral point. Growth of barley on the treated soils failed on account of the high salt content.

RICHARD BRADFELD

The effect of drying soils on the water-soluble constituents. A. F. GUSTAFSON. *Soil Science* 13, 173-214(1922).—A review of the literature is given. Samples of soils of several series and types were taken by driving steel tubes into the soil, then sealing both ends with paraffin to prevent evapn. All samples were stored in a refrigerator at 8-12° in order to minimize bacterial activity. 100 g. of soil calcd. on a H_2O -free basis (105°) were treated with 500 cc. H_2O and the amt. of salt going into soln. was detd. by evapn. an aliquot to dryness (105°) and weighing. Air drying increased the amt. of water sol. material in many cases several hundred per cent. Oven drying at 105° caused a still larger increase. The increase was in general greater in the more highly colloidal soils. Oven drying decreased the nitrate content of these soils. The studies show the necessity of keeping soils to be used for scientific studies under conditions strictly comparable as to aeration, moisture content and temp. in order to avoid the introduction of uncontrolled factors which might lead to erroneous conclusions.

RICHARD BRADFELD

Apparent infertility of the soil around trees. C. O. WILLIAMS. *J. Dept. Agr. Union S. Africa* 5, 254-8(1922).—The exptl. evidence indicates that the apparent infertility of soil in close proximity to growing trees may be due, in part, to depletion of the soil moisture by the tree itself. Following a heavy storm and a week of dry weather samples of soil were taken from a clean field at a distance of 0, 5, 10 and 20 yards from the trees. These samples were immediately analyzed for capillary moisture. The results showed a steady increase in capillary moisture as the distance from the tree increased until at 20 yards the increase over that found immediately beneath the trees was 80% for the first 9 in., 41% for the second 9 in., and 47% for the third 9 in.

K. D. JACOB

Good soil for good roses. S. L. JODIDI. *The Am. Rose Annual* 1922, 101-102.—With favorable environmental conditions, such as ample sunshine, well-protected and adequately drained soil, present, the thing most needed is good texture of the soil and abundance of plant food, since the rose is a heavy feeder. While a clayey soil may essentially be improved both physically and chemically by the addn. of wood ashes, slaked lime, and humus, amelioration of sandy soils can be brought about by the application of org. materials such as manure, peat, muck, mulch, etc. In either case the application of com. fertilizers, such as saltpeper, kainite and superphosphate, may under certain conditions be useful.

S. L. J.

The influence of growing plants upon oxidation processes in the soil. J. P. NZLLER. *Soil Science* 13, 139-61(1922).—The influence of growing roots upon oxidation activities was studied by comparing the amts. of CO_2 evolved from two lots of the same soil, one planted and the other unplanted, with all other conditions, such as moisture, aeration and supply of plant nutrients as nearly as possible the same. The soils were placed in an enclosed system and CO_2 -free air was drawn over them. The free CO_2 liberated was absorbed in $Ba(OH)_2$ and measured; that fixed by the growing plants was measured by analyzing the plants for the total C. The av. total amts. of CO_2 recovered from cultures planted with huckwheat, field peas and soy beans were 118.5%, 70.8% and 60.0% greater, resp., than were the corresponding amts. recovered from unplanted checks. All evidence obtained indicates that growing plants of huckwheat, barley, soy beans and field peas have a beneficial influence upon oxidation activities in the substrata in which the plants are grown and suggests a symbiotic relationship between the soil-oxidizing organisms and the growing green plants. R. B.

The influence of humus acids on cultivated plants. HERMANN FISCHER. *Mitt. deut. Landw.-ges.* 37, 559(1922).—Crop expts. were carried out on a distinctly acid soil. The acidity was considered as being due to humus acids, Ca being present in very small quantities. Potatoes, beets and cabbage showed little injury. Oats, barley, peas and vetch exhibited a strong yellow-green color. The injury to beans and rhubarb appeared in the form of numerous brown spots. Berries, stone fruits, apples, pears, elders and ornamental shrubs were injured to a great extent. Applications of lime and cyanamide proved very beneficial. K. D. JACOB

Inoculation experiments with rye. ERNST ENGELMANN. *Mitt. deut. Landw.-Ges.* 37, 560(1922).—Rye inoculated, previous to planting with a new form of non-corrosive, bacteria-contg. compost was compared with the untreated grain on a loess soil deficient in lime. Both the inoculated and untreated plots received identical applications of N, P_2O_5 and K_2O . The inoculated rye showed an increase of 24% grain and 18% straw over the untreated plots. K. D. JACOB

The periodic influence of season on the course of nitrification. BRUNO SCHÖNBRUNN. *Centr. Bakt. Parasitenk.*, II Abt. 56, 545-65(1922).—Whatever influence the season of the year has on NH_3 formation and nitrification in soils can be explained as the influence of temp. JULIAN H. LEWIS

Alleged toxic effect of chemical fertilizers upon stock. CHAS F. JURITZ. *J. Dept. Agr. Union S. Africa* 5, 208-9(1922).—A brief review. K. D. JACOB

Action of different fertilizers upon the "Vietsbohnen." A. VAN HAUTEN. *J. Landw.* 70, 1-7(1921).—Results are given of the effect of the fertilizers, K, N, P_2O_5 , $K + P_2O_5 + N$, $K + N$, $K + P_2O_5$, and $P_2O_5 + N$, upon the growth and yield of the "Vietsbohnen." A complete chem. analysis of the dry substance and of the ash is given. The plants required no N, and but little P_2O_5 , but the need for K was very great. K plots gave the greatest yield of seed. Plots fertilized with N, P_2O_5 or $P_2O_5 + N$ gave the largest yields of protein. The seeds from all K plots showed the highest starch, fat and ash content. F. M. SCHERTZ

Fermentation and preservation of manure. I. A study of certain bacteria involved in the ammonification of manure. H. J. CONN AND R. C. COLLISON. N. Y. (Geneva) Agr. Expt. Sta., *Bull.* 494, 1-27(1922).—A study of the action on manure of various pure cultures of bacteria showed that of the rapid liquefiers of gelatin investigated, such as *B. cereus* and *Pseudomonas fluorescens*, none are able to give off NH_3 in quantities comparable to that given off from unsterilized manure, and that only one organism has been found which in pure culture and under lab. conditions is capable of giving off ams. of NH_3 from manure equal to or greater than that obtained from unsterilized manure. This organism is a very small, nonspore-forming, non-motile, Gram-negative rod which does not liquefy gelatin or acidify sugars but reduces nitrate quite vigorously to nitrite. No distinct evidence has yet been obtained that it has any actual proteolytic action on the org. matter present in manure. II. A study of certain preservatives and their effect on the fertilizing value of manure. R. C. COLLISON AND H. J. CONN. *Ibid* 23-74.—In lab. and greenhouse investigations of preservatives for manure, acid phosphate and peat were found to be efficient agents for preventing loss of NH_3 either from unsterilized or artificially inoculated manure. Gypsum did not prove as effective in this respect and rock phosphate was still less so. W. H. ROSS

Effect of potash fertilizers on grain in argillaceous and argillo-calcareous land. SCHRIEBAUX. *Compt. rend. acad. agr. France* 8, 613-6(1922).—A discussion of the effect of potash fertilizers on cereals. F. M. SCHERTZ

Nitrogenous fertilizer experiments in Indre and Loire. J. B. MARTIN. *Compt. rend. acad. agr. France* 8, 677-8(1922).—The object of the expt. was to det. the relative

value of cyanamide, a French product. The check plot produced 13.20 cwt. of grain (oats), the nitrate of soda plot, 18.65, the cyanamide plot 18.54, and the $(\text{NH}_4)_2\text{SO}_4$ plot 17.84.

F. M. SCHERTZ

A nitrogen fertilizer experiment on tobacco and observation on plants of the experiment plots. E. BLANCK AND F. PRINGS. *Landw. Ztg. Fühlings* 71, 221-6(1922).—Plants without N were backward in their development. Those supplied with stable manure were best and possessed the greatest leaf growth. Urea produced slightly more growth than did $(\text{NH}_4)_2\text{SO}_4$. Both produced larger yields than did fertilizers without N.

PAUL BOONS

The advantages of the use and production of ammonium bicarbonate for fertilizer purposes. W. GLUUD. *Chem.-Ztg.* 46, 693-7, 715-7(1922).—Field expts. show that on an av. the N of NH_4HCO_3 is only slightly inferior in action to that of $(\text{NH}_4)_2\text{SO}_4$ and in a no. of cases it gave equal and better results. No evidence was obtained of the loss of NH_3 when NH_4HCO_3 was applied to the soil. NH_4HCO_3 has the advantage over $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl in that it adds no acid radical such as SO_4 and Cl and has no tendency to cause a soil to become acid. It is pointed out that continued use of $(\text{NH}_4)_2\text{SO}_4$ tends to fix the soil Ca as CaSO_4 while NH_4Cl causes a loss of soil Ca through washing out as CaCl_2 . NH_4HCO_3 does not possess these disadvantages, and the CO_2 added to the soil is of a distinct benefit to plants. NH_4HCO_3 , when manufactured for fertilizer purposes, is easily drilled and shows no tendency to lump or cake on storage. It should not be compounded with $(\text{NH}_4)_2\text{CO}_3$ in this respect. NH_4HCO_3 develops an odor of NH_3 and loses wt. on storage in sacks or open vessels. 30 kg. NH_4HCO_3 stored in a tight box for 10 months in a cellar showed absolutely no change in wt. Stored in barrels the loss in wt. was 2.75 and 5% for 30 and 50 days, resp.; with 40 kg. of the material stored in paper bags, treated with a soln. of coumarin resin, the loss was only 0.5% in 30 days. The loss of NH_3 and decrease in wt. of NH_4HCO_3 on storage is dependent upon the humidity of the air and the amt. of surface exposed. To prevent possible loss of NH_3 the addn. of drying agents, admixing with superphosphate, or briquetting is advised. The dry salt is stable to 60° and in the presence of H_2O can be heated to 80° with very little loss of NH_3 . Under the latter conditions, however, CO_2 is evolved and the NH_4HCO_3 goes over to the sesquicarbonate, $2\text{NH}_4\text{HCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3$. The machinery and details of the industrial manuf. of NH_4HCO_3 are described.

K. D. JACOB

The phosphoric acid question. KARL VON KUFFNER. *Mitt. deut. Landw.-ges.* 37, 512-3(1922).—Field expts. with certain soils indicate that if the soil contains 0.1% or more of P_2O_5 , the use of P_2O_5 fertilizers is unnecessary, provided the ratio of MgO to CaO , present in the soil, is at least 1:2. If the ratio of MgO to CaO was less than 1:2 application of P_2O_5 fertilizer gave good results.

K. D. JACOB

Action of phosphoric acid on heavily and poorly limed land. AUGUST RIPPEL. *Fühlings Landw. Ztg.* 71, 259-65(1922).—In cereals and kindred crops no larger yields were obtained on heavily limed plots than on those lightly limed. Increased yields were obtained in todder, beets and red clover on well limed fields. R. concludes that whether the field be acid or alk., CaCO_3 plays no role in the removal of P_2O_5 from the soil by plants. Phosphoric acid increased the protein content of grain grown on heavily limed plots.

PAUL BOONS

Answer to the paper of A. v. Nostitz on "The crusting action of magnesia salts." O. NOLTE. *Landw. Vers. Sta.* 99, 293-4.

F. M. SCHERTZ

Further investigation of the exchange acidity of mineral soils. H. LIESEGANG. *Landw. Vers. Sta.* 99, 191-230(1922).—The subjects treated are: exchange acidity in neutral soils by acids; exchange acidity by Al and Fe chloride solns.; exchange acidity in natural soils by CO_2 ; production of exchange acidity by permutter; exchange acidity

and mol. relation of silicic acid, argillaceous earth and bases according to Gans; detn. of the requisite amt. of lime to prevent exchange acidity. F. M. SCHERTZ

Ammonia as the beginning and end product of nitrogen exchange in plants. PRIANISCHNIKOW. *Landw. Vers. Sta.* 99, 267-88(1922).—Expts. with *Vicia sativa* and *Zea mays* are reported and tabulated as follows:

	Exptl. conditions.		Results asparagine synthesis.	NH ₃ accu- mulation.
	carbo- hydrate.	light.		
1	+	—	+	—
2	—	—	—	+
3	+	+	+	—
4	—	+	—	+

Hence, asparagine synthesis is conditioned by the presence of carbohydrates.

F. M. SCHERTZ

The manufacture of double superphosphate and the preparation of sodium phosphate. H. VOSS. *Chem.-Ztg.* 46, 581-3, 606-9(1922).—The possible chem. reactions occurring in the manuf. of superphosphate and double-superphosphate by the action of H₂SO₄ on phosphate rock are discussed in detail. The method of calcg. the quantity of H₂SO₄ necessary to give the desired reactions with phosphate rock of known compn., as well as the proportion of end-products obtained, is illustrated by examples. The different steps in the process of manuf. are detailed and the necessary machinery is described. The manuf. of Na₂HPO₄ from H₂PO₄ and Na₂CO₃ is briefly described.

K. D. JACOB

The significance of the physiological mineral salts in nature. W. PFELDER. *Mitt. deut. Landw.-ges.* 37, 542-3(1922).—A general discussion of the effect of certain mineral salts on animals, plants and bacteria.

K. D. JACOB

The story of phosphate rock. ANON. *Am. Fertilizer* 57, No. 10, 23-38(1922).—An illustrated statistical review of the distribution and character of phosphate deposits, and of the manuf. of acid phosphate.

W. H. ROSS

Possibilities in the use and preparation of concentrated fertilizers. WM. H. ROSS. *Am. Fertilizer* 57, No. 10, 39, 40, 63-4(1922).—A discussion of the possibility of using concd. materials as fertilizers with a view to developing new sources of fertilizers such as that furnished by N-fixation, and to reducing the expense of handling and transporting fertilizers which require shipment to a distance.

W. H. ROSS

Experiments with spray solutions for preventing insect injury to green logs. F. C. CRAIGHHEAD. U. S. Dept. Agr., *Bull.* 1079, 1-11(1922).—Creosote oil alone, or mixed with different proportions of kerosene, gave best results in a preliminary study of the use of various poisons for preventing insect attack to crude forest products such as green saw logs and timbers employed in rustic construction.

W. H. ROSS

The formation of calcium cyanamide from calcium ferrocyanide. HEINRICH PINCASS. *Chem.-Ztg.* 46, 661(1922); cf. *C. A.* 16, 2455.—By heating Ca₂Fe(CN)₆, CaCN₂ is produced in the dry way according to the following equation Ca₂Fe(CN)₆ = N₂ + FeC₂ + 2CaCN₂ + C₂. At a temp. of 630° both ferrocyanide and cyanamide ions are present. At 690° the Ca₂Fe(CN)₆ is completely decomposed. The best yield of CaCN₂, 89%, was obtained by heating at 690° for 69 min. With higher temps. and longer heating the yield decreases.

K. D. JACOB

Determination of total nitrogen in cyanamide and nitrate mixtures—Davisson-Parsons method. K. D. JACOB AND W. J. GELDARD. *J. Ind. Eng. Chem.* 14, 1045-6(1922).—Comparative studies of methods for the detn. of total N in cyanamide and nitrate mixts. show the Davisson-Parsons method to be highly satisfactory. This method is also applicable to aq. exts. The Gunning-Forster and the modified Gunning

methods, which were used in comparison, were lower and less concordant in most cases.

M. S. ANDERSON

Graphitic nature of the carbon of lime nitrogen. N. KAMEYAMA. *J. Coll. Eng. Tokyo Imp. Univ.* 11, 111-23(1922).—This is an English edition of the paper abstracted from the Japanese in *C. A.* 16, 2389.

E. H.

The cause of nitrogen loss in urine, excrement and other organic substances. OTTO NOLTE. *Landw. Vers. Sta.* 99, 287-92(1922).—A review.

F. M. SCHERTZ

Preliminary studies on the isolation of sulfur-oxidizing bacteria from sulfur-floats-soil composts. J. S. JOFFE. *Soil Science* 13, 161-72(1922).—Various culture media were inoculated with a sulfur-floats-soil compost known to contain S-oxidizing organisms. Most of these proved unsatisfactory. The following combination gave the best results: K_2HPO_4 5 g., NH_4Cl 2.0 g., dextrose 1 g., $MgSO_4$ 5 g., S 10.0 g., $FeCl_3$ 2-3 drops of a 10% soln., H_2O 1000 cc. In the earlier stages of the cultures, fungi, especially mucor and fusarium, appeared on plating but on long incubation and transfer they disappeared leaving only minute bacteria. Reactions as low as p_H 1.2 were obtained, 48% of the S being oxidized to H_2SO_4 in 150 days. The largest amt. of sol. phosphates was obtained with a combination of the most effective single cultures, indicating a possible associative action of fungi and bacteria in the oxidation of S in the soil.

RICHARD BRADFELD

Combating the field mouse. SCHWANDER AND R. MEYER. *Mitt. deut. Landw.-ges.* 37, 522-4(1922).—Lab. expts. on the action of different chem. compds. on field mice are briefly reviewed. Salts of Ba, As, Cu, Hg, compds. of P, and cyanamide, dicyanodiamide, H_2S , CS_2 , and strychnine were used. $BaCO_3$ and strychnine appeared to give the best results.

K. D. JACOB

The constitution of basic slag (SCOTT, MCARTHUR) 9. By-products of industrial abattoirs, modern butchering installations and the utilization of animal blood (A. B.) 12. Fertilizing value of activated sludge (BROWN) 14.

Fertilizers. J. GRADL. *Brit.* 184,800, Aug. 15, 1922. A fertilizer consists of finely divided or colloidal C or carbonized org. material in admixt. with one or more oxidizers or catalysts or with both. Other fertilizing substances may be added. K , NH_4 , and other nitrates are preferably used as oxidizers. MnO_2 and other compds. of Mn, clay and other compds. of Al, MgO and other compds. of Mg are the preferred catalysts. The C may be obtained by treating sawdust, peat, sea-weed, "humus-lignite," or sulfite lye with SO_2 and utilizing the resulting H_2SO_4 to break down raw phosphates.

Fertilizers. J. GRADL. *Brit.* 185,729, Aug. 22, 1922. Addition to 184,800 (preceding abstract). The method of the principal patent is modified in that the org. materials are not carbonized. Peat, "humus-lignite," wood-flour, and algae are mentioned as suitable materials. The admixt. of the catalysts and oxidizing agents or other fertilizers may be combined in one operation with the comminution of the org. raw material.

Fertilizers. D. LO MONACO. *Brit.* 184,833, April 7, 1921. The process for the treatment of humus with halogen gas, described in 159,481 (*C. A.* 15, 2147), is applied to other nitrogenous org. fertilizing materials, such as manure, rubbish, refuse, oil seed cakes, ricinus, colza, lemon refuse, ground horn and nails, dried blood, chrysalids, bones, leather chippings, and cloth refuse. The treatment may be carried out in a closed casing fitted with an agitator. Cf. 2662, 1873 and 4103, 1875.

Vermin-destroying, etc., compositions. P. CALOVI. *Brit.* 184,929, June 13, 1921. A process for making an adhesive compd., particularly for destroying vermin, consists

in beating raw linseed oil until it thickens to a rubber-like state, when it is stirred into reddish lumps. H_2O is then added and the mass stirred until the lumps disappear. A small portion of this mixt. is heated with resin and is poured back into the original mixt. of oil and H_2O at intervals. The resultant mixt. of oil, H_2O , and resin is spread on a table to cool.

16—THE FERMENTATION INDUSTRIES

C. N. FREY

The importance of colloid chemistry to the fermentation industry. H. FÄRUND-LICH. *Z. angew. Chem.* 35, 517-9(1922).—A discussion is given of some of the principles of colloid chemistry and their application to the fermentation industries. Fermentation is a biological-chemical problem in which colloid chemistry plays an important part. Most of the changes in beer, a colloidal solution, may be explained on the basis of colloidal behavior. Colloids are also concerned with foaming and with the CO_2 retention of beer. Substances toxic to yeast, such as phenol and $HgCl_2$, may be adsorbed by the cell colloids. That the fermenting activity of yeast is inhibited by small aunts. of Am, Bu or nonyl alc. may be explained by assuming that these substances alter the surface tension, accumulate at the surface of the cells and thus displace sugar.

C. N. FREY

Manufacture of industrial alcohol and alcohol motor fuel in the Philippine Islands. *Philippine J. Sci.* 21, 17-48(1922).—The most abundant raw materials are cane molasses and the juices of various palms, that of the nipa palm being the cheapest of all sources. The use of alc. mixts. as motor fuels is discussed in a general way and a bibliography is given. The harvesting of nipa and coco palm juices is described in detail. L. E. G.

Fermentation of cherries with pure yeasts. KARL SCHWEIZER AND HERMANN FISCHLIN. *Mitt. Lebensm. Hyg.* 13, 217-22(1922).—Good fermentation products are obtained with *Saccharomyces Cerasi* I, *Cerasi* II, *Chodati* and *Fischlinii* (all 4 by Schweizer) while a poor brandy results with *S. Zoffii* Artari.

H. A. LEPPER

Study of the causation of "ropiness" in worts and beers. P. HAMPSHIRE. *Bull. Bur. Bio-tech.* No. 6, 179-87(1922).—A new species of bacterium was isolated from a pitching yeast and found to cause typical ropiness, with mucilage and slime, in beers. This bacterium is closely allied to the *Acetobacter* and functions best when the O supply is strictly limited.

F. L. SEYMOUR-JONES

"Speckled" malt. F. A. MASON AND F. BROWN. *Bull. Bur. Bio-tech.* No. 6, 188-91(1922).—The black banded grains ("magpies") of speckled malt were compared with sound malt from the same sample. The samples gave the same H-ion concn., sp. rotation, and brewer's ext.; the speckled showed a darker color and a slightly higher titrable acidity. Except for an increase of tint, the brewing value of a malt is not affected by the presence of speckled grains.

F. L. SEYMOUR-JONES

Modern malting apparatus. Gg. ILLERT. *Chem. App.* 9, 179-82, 192-4, 201-3 (1922).—A description of the arrangement and operation of the plant, with 11 cuts of app.

J. H. MOORE

The chemical composition and the bouquet of wines. P. MALVEZIN. *Ann. chim. anal. chim. appl.* 4, 298, 301(1922).—The so-called bouquet of wines is merely the combined taste and odor sensation of certain odorous substances in soln. It is an evidence of the aging and other qualities of the liquor, e. g., the relative proportion of $AcOEt$ present as shown by the taste and odor is indicative of the maturity of wine, the $AcOEt$ being formed by the slow combination of $EtOH$ and $AcOH$ up to the equil. point. A resumé is given of the "aromatophore" theory of odor as proposed by Klimont, Cohn and others.

W. L. OWEN

The action of metals on sulfited wines. P. GEFLOT. *Ann. fals.* 15, 326-30(1922).—When Cu, Ni, or Pb is added to wine contg. not over 450 mg. of SO_2 per l. it does not become turbid. With Pb it retains its color; but with Cu or Ni it becomes more or less green, CuS or NiS is deposited, and CuSO_4 or NiSO_4 dissolves out. Pb dissolves as PbSO_4 . With these metals a soln. contg. 27.2 g. SO_2 per l. became turbid very slowly. Ag did not react even when boiled with a soln. contg. 27.2 g. SO_2 per l. In the presence of as little as 25 mg. SO_2 per l., Fe and Zn rapidly, Al and Sn much more slowly, cause the wine to become turbid, with evolution of H_2S . Part of the metal is transformed into sulfide and part dissolves as sulfate. The metal forms sulfite and H_2SO_3 . The latter is fixed by the aldehydes of the wine, and the excess decomposes to H_2S , S, sulfides, and ultimately sulfates. The results obtained on wine were confirmed by working on a dil. alc. soln. contg. SO_2 . A. P.-C.

The determination of free and combined volatile acids in wine. PHILIPPE MAL-VAZIN. *Ann. fals.* 15, 360-2(1922).—Polenical against Ferré (cf. C. A. 16, 2754).

A. P.-C.

Alcohol denaturants. N. H. JOHANSSON. Brit. 185,126, Aug. 25, 1922. Alc. is denatured by adding unsatd. C compds. contg. an aldehyde group. These compds. may be produced from lower aldehydes, by "aldol" condensation and subsequent dehydration by distn. or otherwise. The aldehydes may be obtained from alc. or from C_2H_2 and water. Thus, crotonaldehyde is produced from EtOH , and tigaldehyde from AcH and propionaldehyde. Highly unsatd. aldehydes, such as "hexadienals," are formed by further condensation between AcH and products already formed.

Flavoring and coloring materials for beer. F. VYDRA. Brit. 184,381, Aug. 19, 1921. A flavoring and coloring material for beer is made by mashing and saccharifying ground or bruised barley or other malt in the ordinary way, concg. the saccharified mash on a water bath, by steam heating, or *in vacuo*, and kiln drying the concd. residue at 110° .

17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Detection of extract of *Atractylis gummifera* (masticogna) in extract of liquorice. UGO GIUFFRÈ. *Boll. chim. farm.* 61, 609-11(1922).—The adulteration of ext. of liquorice with ext. of *Atractylis gummifera* is becoming a common practice in Sicily and threatens to bring the product into commercial disrepute, being due particularly to the addition of a poisonous glucoside. The detection of *Atractylis gummifera* is based upon the identification of valeric acid by its odor and a delicate color reaction for atractiligin. Dissolve 50 g. of sample in a small vol. of hot H_2O . Add 500 cc. EtOH which ppt. pectins, gums, etc. Treat with animal charcoal and filter. Evap. the filtrate to a small vol., dil. with a little H_2O and make alk. with NaOH . Reflux 0.5 hr., cool, acidify with H_2SO_4 and distil with steam. The odor of valeric acid in the distillate indicates adulteration. If the odor is not characteristic, neutralize the distillate with NaOH , evap. to dryness and treat the residue with EtOH and H_2SO_4 . The odor of BuCO_2Et is easily detected. Sat. the residue from the 1st distn. with $(\text{NH}_4)_2\text{SO}_4$, add EtOH , decolorize with charcoal and filter. Evap. the filtrate, add H_2O and filter. Dissolve the ppt. in EtOH , reflux with charcoal, filter and concd. to a small vol. Evap. a drop of this concd. ext. to dryness on a watch glass and treat with a few drops of concd. H_2SO_4 . If atractiligin is present the yellowish color changes to carmine red on the addition of an aq. soln. of piperonal or vanillin. A. W. Dox

Matriculation sheets. A. SCHAMELROUT. *J. pharm. Belg.* 4, 686, 726, 742(1922).—

Monographs intended for the Belgian National Formulary are given for cryst. quassin, Na cacodylate, birch tar and pyridine.

A. G. DuMéz

Method of the French Codex for the detection of iodates in potassium iodide. LACHARTRE. *Repert. pharm.* 34, 261-3(1922).—L. calls attention to the fact that the Codex does not give definite directions in the test for iodates in KI with respect to (1) the degree of diln. of the iodide soln., (2) the quantity of AcOH to be used in acidifying the soln., or (3) the time at which the color change should be observed. If a satd. soln. of KI is used, the CHCl_3 will not ext. the free I and will, therefore, not give the color reaction. A 10% soln. is the most satisfactory, but even then the test is only sensitive to 80 mg. of iodates per kg. of KI. The 10% soln. has the further advantage that it is not altered by air free from CO_2 and only slowly when the latter is present. If protected from the light, the soln. will not turn yellow within 2 mos. The time of observing the color change is important as exposure to the air of the acidified soln. will result in the liberation of I from the KI. To overcome the above deficiencies, L. recommends that the test be worded as follows: "Dissolve 1 g. of KI in 10 cc. of recently boiled distd. H_2O , add 3 cc. of CHCl_3 , followed by 5 drops of cryst. AcOH and shake for $\frac{1}{2}$ min. At the end of this time, the CHCl_3 layer should not be rose colored."

A. G. DuMéz

Heavy magnesium oxide. CABANNES. *Repert. pharm.* 34, 289(1922).—C. examd. a sample of calcined magnesite which was especially compact and heavy, and a pale rose in color instead of white. Fe was present, from which it is concluded that the product was prepd. by calcining dolomite instead of pptd. MgCO_3 .

A. G. D.

Capsella bursa pastoris Moench. R. WASICKY. *Ber. pharm. Ges.* 32, 142-58(1922).—An investigation undertaken to settle the question whether the *Capsella* plant, in its several stages of development in both infected and fungus-free condition, could replace ergot yielded evidence in the negative.

W. O. E.

Colloidal nature of saccharated ferric oxide. C. MANNICH AND C. A. ROJAHN. *Ber. pharm. Ges.* 32, 158-66(1922).—The paper describes among other things expts. tending clearly to demonstrate the colloidal nature of a saccharated ferric oxide soln. The soln. gave the Tyndall phenomenon, and after filtration the perfectly clear liquid showed under the ultramicroscope innumerable submicrons. On electro-cataphoresis, the colloid particles move toward the anode, i. e., are negatively charged. Particles of iron oxychloride soln. are positively charged.

W. O. E.

Pregl's solution. M. BACHSTEZ. *Ber. pharm. Ges.* 32, 216-21(1922); cf. HERRMANN, *Apoth. Ztg.* 37, 203.—Pregl's soln. is not essentially a hypoiodite soln. It is a soln. of KI and NaIO_3 , together with a little NaCl and NaHCO_3 in order to render it isotonic. It has no const. compn., a fact explanatory of the divergent results obtained by different investigators.

W. O. E.

Standardization of disinfectants. K. RUELKE. *Chem.-Ztg.* 46, 897-8(1922).—R. suggests representing a disinfectant by means of 2 curves, the one indicating the germicidal power at 17.5° , the other the antiseptic power under the usual conditions of procedure. The present methods of standardization are inadequate.

W. O. E.

Determination of the so-called total geraniol content of citronella oil. A. W. K. DEJONG AND A. RECLAIRE. *Perfumery Essent. Oil Record* 13, 319-21(1922).—In the course of this research it was observed that an exact measuring of the KOH is of paramount importance, and best effected by using an automatic filling pipet provided with a 2-way cock (illustrated in the original). The detn. is carried out substantially as follows: Mix 10 cc. of the sample (dried over anhydrous Na_2SO_4) with 10 cc. Ac_2O of about 80%, 2 g. NaOAc and some pieces of porous plate in a 100 cc. flask, and reflux gently on a sand or air bath for 2 hrs. After cooling, add about 50 cc. H_2O , and heat

with reflux over a boiling H_2O bath 15 min. with occasional shaking. Transfer the product to a separator, wash with brine until neutral, dry over anhydrous Na_2SO_4 , and filter. Weigh out in mg. 1.5 g. of the acetylated oil in a 100 cc. flask, add 2 cc. neutral $EtOH$, neutralizing any acid possibly present with 0.5 N alc. KOH in the presence of phenolphthalein, finally adding 20 cc. 0.5 N alc. KOH and some pieces of porous plate. Boil on a H_2O bath in connection with an air condenser for 2 hours, allow to cool, add 50 cc. H_2O , titrating the excess of KOH with 0.5 N H_2SO_4 . W. O. E.

Commercial eucalyptus oils and derived products. ANON. *Perfumery Essent. Oil Record* 13, 324-8(1922).—Mention is made of Baker and Smith's work, "A Research on the Eucalypts and their Essential Oils," (cf. *C. A.* 15, 1190) in which 177 species are described, but of these only about 14 are distd. for oil. The paper is mainly a summary of the sources and characters of these oils prepd. by A. R. Penfold. W. O. E.

Properties and preparation of Dutch East Indies sandalwood oil. A. ROJDESKY-WEISKY. *Perfumery Essent. Oil Record* 13, 331-2(1922).—The yield of Dutch Indian sandalwood oil varies from 3.8 to 5.8%, that from Macassar having the following characters: d_{20}^{20} 0.9745-0.9842; $n_{D,20}^{20}$ $-16^{\circ}40'$ to $18^{\circ}40'$; santalol 93.7-98%; sol. in any vol. of 90% alc.; $n_{D,20}^{20}$ 1.500 to 1.5013. W. O. E.

Simple method for estimating free phosphorus in phosphorated oils. O. FRY. *Pharm. Monatshefte* 3, 101-2(1922).—Into a 200-g. medicine bottle weigh accurately about 1.5 g. of the sample, dissolve in a mixt. of 10 g. 96% $EtOH$ and 30 g. Et_2O , adding from a pipet 20 cc. 0.1 N I soln., then close the flask and shake vigorously for 2 min. Run a control in a 2nd flask contg. all the above ingredients except the oil. Titrate the I excess in both cases with 0.1 N $Na_2S_2O_3$. One cc. of 0.1 N $Na_2S_2O_3$ = 0.001033 g. free P. W. O. E.

Properties of potassium permanganate, and the German Pharmacopeia. G. FETTER AND G. BRUDE. *Z. angew. Chem.* 35, 527(1922).—The original bronze-brown color of $KMnO_4$ crystals by virtue of superficial decompn. from the action of atm. CO_2 and org. dust passes through violet to steel-blue, the upper layer hereby acting as a filter and protection to those below. These color changes are very rapid when the crystals are surrounded by the vapors of mineral acids and in the presence of light. The pharmacopoeial description should therefore be changed; that suggested for the German is: "Dry bronze-brown crystals with metallic luster, assuming in the air a violet to steel-blue color." It would be more accurate to characterize the crystals as "rhombic-bipyramidal" or simply "rhombic," in view of the popular conception of the term "prisms" as meaning exclusively elongated individual crystals. Finally, suitable revision should be made in statements referring to the stability of $KMnO_4$ in dil. (1 + 999) soln. in contact with litmus and other org. matter. W. O. E.

The chemistry of cosmetic ointments and of glycerol. E. UNNA. *Z. deut. Oel-Fett-Ind.* 42, 542-50(1922).—A general discussion of the use, prepn. and physiological action of the various ointments, under the following captions: I. Introduction. II. Fatty ointments and pastes. (1) Reducing ointments. (a) Drying pastes. (b) Tar-casein pastes. (c) Composite and Wilkinson ointment. (d) Scaling compounds. (e) Pyrogallol and resorcinol sticks. (f) Arsenical salves. (2) Oxygen salves. (3) Covering pastes. (a) Alum pastes. (b) Bismuth oxychloride paste. (c) Bolus powder pastes. (4) Glycerol. (5) Aqueous salves and pastes. (6) Air pastes. P. E.

Modern preparations for the care of the mouth. LEGRADI. *Z. deut. Oel-Fett-Ind.* 42, 550-2(1922).—A brief account of the growing knowledge in the care of teeth with reference to tooth-pastes and mouth-washes. The present view of tooth caries considers it to be result of bacterial action, mainly streptococci. The acid reaction of the saliva is of no importance except where food remnants in inaccessible places produce acids and aid bacterial growth. P. E.

Different methods of curing tobacco. J. v. P. OOSTHUIZEN. *J. Dept. Agr. Union S. Africa* 5, 131-50(1922).—The different methods are described and discussed. The chem. and mech. changes occurring in the leaf during drying are also indicated.

K. D. JACOB

The need for an improved formula for infusion of digitalis. A. R. BLISS, JR. *J. Am. Pharm. Assoc.* 10, 757-60(1921).—The method of assay used was the Hatcher and Brody method (*C. A.* 4, 3279). Fifteen samples of infusion of digitalis selected at random from retail drug stores showed an av. activity of 46.26% of theory. Five of these samples had been prepd. by diln. of the fluidext. instead of by the U. S. P. method. These five showed an av. activity of 62.6% of theory. Five samples prepd. by the Hatcher and Eggleston method (*C. A.* 10, 367) showed an av. activity of 95%. The need for an improved U. S. P. method is apparent. The H. and E. method is recommended. The tincture of digitalis is satisfactory for most purposes and the infusion might be dropped without loss to therapy.

L. E. WARREN

The relative action of preservatives in pharmaceutical preparations. L. F. GABEL. *J. Am. Pharm. Assoc.* 10, 767-8(1921).—An acid soln. was prepd. from senna 1 oz., sucrose 1 oz. and H₂O to make 1 pt. An alk. soln. was prepd. from beef ext. 1 oz., sucrose 1 oz., NaHCO₃ 140 grains and H₂O to make 1 pt. A neutral soln. was like the alk. soln. but minus the NaHCO₃. Portions from each soln. were tested separately with varying amts. of different preservatives. Each expt. was inoculated with a gas-producing bacterium and the temp. kept at 90° to 98° F. The preservatives found to be inferior were H₃BO₃, cinnamic acid, SO₂, Na salicylate, NaHSO₄, Na benzoate, CHCl₃, and chlorobutanol. Benzoic acid, salicylic acid, C₆H₅(OH), EtOH and CH₂O were found to be the best. Benzoic acid was more effective than salicylic acid, although neither was satisfactory in alk. media. With CH₂O 3.84 minims of the 37% soln. to the pt. were sufficient. With EtOH 15% was necessary in acid, 17.5% in alk. media.

L. E. WARREN

The estimation of nitroglycerin in tablets of nitroglycerin and spirit of nitroglycerin. R. I. GRANTHAM. *J. Am. Pharm. Assoc.* 10, 840-3(1921).—Five methods were considered. G. has adapted the Devarda method (for N in nitrates) to the detn. of C₃H₅(NO₃)₃. Tablets equiv. to about 0.065 g. of C₃H₅(NO₃)₃ are powdered, shaken with 50 cc. of Et₂O for 1 hr., the mixt. is filtered, 25 cc. of the filtrate treated for 10 min. with 15 cc. of 0.1 N KOH in EtOH, after which 10 cc. of 3% H₂O₂ are added. The container is covered with a watch glass and the mixt. slowly heated on a water bath until the Et₂O and most of the EtOH have been dissipated. The residue is transferred to an 800 cc. Kjeldahl flask, H₂O added to make about 250 cc. and 2 g. of the Devarda alloy and 5 cc. of concd. NaOH are added. The mixt. is boiled for 30 min.; then steam is passed through the mixt. and the vapors are passed through a Davison scrubber before going into the condenser. The NH₃ is collected in a measured vol. of standard acid and the excess titrated back in the usual way. The method gives good results.

L. E. WARREN

The alkaloidal standard of fluidextract of ipecac U. S. P. FRANTZ F. BERG. *J. Am. Pharm. Assoc.* 10, 848-9(1921).—The U. S. P. standard is now from 1.8 to 2.2 g. of alkaloids per 100 cc., while the U. S. P. VIII standard was 1.5 g. The menstruum in the U. S. P. VIII was 71% EtOH, while in the present edition it is 37%. Ipecac contains much pectinous material. This ppts. in presence of 37% EtOH and carries down some of the ipecac alkaloids, but expts. show that this is not the cause of the low yield of alkaloids as much as is the insoly. of the alkaloids in 37% EtOH. B. recommends that the U. S. P. VIII standard be reinstated.

L. E. WARREN

Tablets for the national formulary. CLYDE M. SNOW AND BERNARD FANTUS. *J. Am. Pharm. Assoc.* 10, 850-4(1921).—Several formulas are suggested with directions for making.

L. E. WARREN

Compound solution of sodium phosphate N. F. H. M. FASER. *J. Am. Pharm. Assoc.* 10, 854-5(1921).—The N. F. formula requires that the $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ used in the prepn. of this soln. should not be effloresced. On standing the N. F. product tends to form crystals. F. recommends the use of an equiv. amt. of the dried salt. A product so made keeps indefinitely.

L. E. WARREN

Domestic and imported *Veratrum* (hellebore), *Veratrum viride* Ait., *Veratrum californicum* Durand and *Veratrum album* L. II. Chemical studies. ARNO VIRHOEVER AND JOSEPH CLYVENGER. *J. Am. Pharm. Assoc.* 11, 166-74(1922).—The alkaloids from *V. californicum* have not been previously reported. V. and C. used the following modification of the Bredeman method for the extn. of the alkaloids. To 15 g. of the drug (No. 40 powder) in a 250-cc. flask add 150 cc. of a mixt. of equal vols. of CHCl_3 and Et_2O , allow to stand 10 min. Add 10 cc. of 10% NH_4OH and shake at intervals for 60 min., add 10 cc. of H_2O , shake strongly, allow to settle, decant through cotton into a flask contg. about 0.25 g. of calcined MgO . Shake and filter into a 100-cc. graduated cylinder. Shake out 80 cc. of the filtrate with 20, 20, 10 and 10 cc., resp., of 10% $\text{C}_6\text{H}_5\text{O}_4$. Collect the acid portions, make alk. with NH_4OH and shake successively with 20, 20, 10 and 10-cc. portions of $\text{CHCl}_3 + \text{Et}_2\text{O}$ mixt., evap. the solvent in a current of air, dry the residue at 100° and weigh. The drugs examd. were variable as to the relative proportions of rhizomes and roots, but the amts. of alkaloid do not vary much in the two species *album* and *viride*.

L. E. WARREN

The manufacture of anhydrous and hydrous wool fat (EHMANN) 27.

Synthetic drugs. SOC. ANON. POUR L'INDUSTRIE CHIMIQUE A BALS. Brit. 184,625, June 7, 1921. Dialkylamides of nicotinic acid are obtained by treating the acid, or its halide, or an ester thereof, with a dialkylamine; they are of therapeutic value. Examples are given of the prepn. of the dimethylamide, dipropylamide, and the piperidide from nicotinic acid chloride or bromide and the hydrochlorides or hydrobromides of the corresponding amines. Nicotinic acid chloride is obtained from the acid in known manner by means of thionyl chloride.

Synthetic drugs. ETABLISSEMENTS POULENC FRÈRES. Brit. 185,723, Aug. 17, 1922. Aminobenzenearsonic acids and their substitution products are prepd. by reduction of the corresponding nitro compds. with a reducing sugar in alk. soln.

Synthetic drugs. C. F. BORRINGER & SOEHNE. Brit. 183,454, July 15, 1922. Anthranilic acid derivs. substituted in the amino group are obtained by treating anthranilic acid or its derivs. or substitution products with either a quinolinecarboxylic acid halide or with a chloroquinolinecarboxylic acid or with a corresponding substituted quinolinecarboxylic acid. The product may be further converted into mono- or dialkyl esters and is of value in the treatment of gout. According to example: 2-phenylquinoline-4-carboxylic acid is converted into its chloride by thionyl chloride or other adsorbent substance.

Emulsions of perfume and flavoring bases. PLAUSON'S (PARENT Co.), LTD. Brit. 184,534, April 11, 1921. Emulsions in H_2O of essential and ethereal oils and like perfume or flavoring bases or of constituents thereof, such as salol, are made by disintegration in a colloid mill such as that described in 155,836, in presence of a dispersator or a protective colloid. In place of H_2O , other immiscible liquid such as glycerol or a mixt. of glycerol and H_2O may be used. Suitable dispersators, i. e., substances capable of accelerating dispersion, are ketones, alcs., and esters and compds. contg. sulfo groups, e. g., Turkey red oil, sulfonaphthenic acids, purified sulfite cellulose liquor. The products are colloidal dispersions, generally transparent. Cf. 29,451, 1897.

Ichthyol. PLAUSON'S (PARENT Co.), LTD. Brit. 184,292, May 21, 1921. Fossil-

ized fish shale, sulfurized shale, and fossils contg. S are treated to obtain ichthyol oil and preps. by high-speed mech. disintegration in the presence of a liquid, preferably H_2O , at a peripheral speed of over 1000 m. per min., preferably in a colloid mill as described in 155,836. Protective colloids may be added, in which case the emulsions obtained are permanent and are suitable for therapeutic use. The oil may be sepd. from the emulsion by heating to 60-70°, with or without the addn. of an electrolyte, or by centrifuging. The oil may then be purified by extrn. with an org. solvent, filtration, and evapn. of the solvent.

18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

Salt industry of Poland. *Chem. Trade J.* 71, 327(1922).—The salt production of Poland is steadily increasing. Statistics are given. O. P. R. OGILVIE

Purifying sodium hyposulfite. A modification of Jellinek's method. W. G. CHRISTIANSEN AND A. J. NORTON. *J. Ind. Eng. Chem.* 14, 1128-8(1922).—An app. is developed for purifying $Na_2S_2O_4$ involving a modification of Jellinek's method (C. A. 5, 2041-2), whereby a 42% yield of $Na_2S_2O_4$ of 98.3% purity from 85% pure salt can be obtained in 4.5 hrs. In principle the procedure consists in satg. an aq. $Na_2S_2O_4$ soln. with NaCl and dehydrating and drying the pptd. $Na_2S_2O_4 \cdot 2H_2O$. All manipulations must be *in vacuo* or in a CO_2 atm. For the analysis of $Na_2S_2O_4$, the Cu method (cf. C. A. 15, 2045) gave low and the Ag method (cf. C. A. 15, 3799) high results. The $K_2Fe(CN)_6$ method (cf. C. A. 14, 3036) was more accurate than either, checking to 2 parts per 1000. The stability of $Na_2S_2O_4$ varies indirectly with the fineness. A combined filtering and stirring device in the app. is suggested for more general use. C. C. DAVIS

The "metallurgy" of tellurium in the wet way. PIERRE HULOT. *Bull. soc. chim.* 29, 1070-1(1921).—Anhydrous K_2TeO_4 is prepd. by fusing H_2TeO_4 with KNO_3 as described in C. A. 14, 1269. To prep. Te from this salt use an alkali and Al, rather than HCl and Zn. In practice 200 cc. of 20% NaOH or KOH and 20 g. of pure Al are added to 30 g. of the salt. The process can be equally well applied to the mineral tetradymite.

G. R. FONDA

Possible innovations in the method of production of sulfur in Sicily. E. CORTESA. *Rass. min.* 57, 40-2(1922).—Only a fundamental change in methods will save Sicilian S production from ruin. It is deemed impracticable to use heat from any direct source of combustion for recovering S, and it is suggested that superheated steam, according to the principle of the Frasch process, be utilized for extrn. C. C. DAVIS

The manufacture of hydrogen by the partial liquefaction of water gas and coke-oven gas. GEORGES CLAUDE. *Trans. Faraday Soc.* (advance proof) Oct. 16, 1922; *J. Ind. Eng. Chem.* 14, 1118-9; *Engineering* 114, 506-7(1922).—See C. A. 16, 993.

E. H.

Technic of the use of liquid chlorine. HENRI BARTHÉLÉMY. *Rev. prod. chim.* 25, 649-52(1922).—A description of the equipment required for obtaining a const. flow of Cl from cylinders or drums. A. P.-C.

Bauxite: Occurrence, mining and uses. R. B. LADOO. *Eng. Mining J.* 114, 805-9(1922).

E. H.

Development of the asbestos industry. *Mining J.* 138, 664(1922).—Canada produces about 80% of the world's supply. Russia has fallen out and Rhodesia and the Union of South Africa have more than taken her place. A history is given and uses are described. *Production statistics* of the various countries from 1913 to 1918 are given. O. P. R. OGILVIE

Adhesives. *Raw Materials Review* 1, 180(1922).—In a process by P. Schrott

(Germany) an agglutinant for veneer is prepd. by mixing lenzin (an impure gypsum), H_2O , a small amt. of ocher, and leather glue which has been soaked in H_2O for about 14 hrs.

O. P. R. OGILVIE

The mechanical properties of chrome-vanadium steels (for nitrogen-fixation apparatus) (VANICK) 9.

Sulfuric acid. T. SCHMIEDL. Brit. 184,966, July 12, 1921. In an ordinary lead-chamber system, the Glover tower is replaced by a mech. app. by means of which the gases contg. SO_2 are brought into intimate contact with finely divided $HNOSO_4$ or H_2SO_4 contg. HNO_3 . The app., which is made of acidproof material, consists of a box-like reaction chamber in which rotate one or more rollers, such as are described in 149,647. The usual Glover reactions are effected whether the gases are hot or cold. Cf. 149,648 (C. A. 15, 414).

Hydrocyanic acid. AIR REDUCTION CO., INC. Brit. 183,348, July 6, 1921. Hydrocyanic acid, which may be absorbed in alkalies to obtain pure cyanides, or may be liquefied, is obtained from pure or crude cyanides by treatment with CO_2 or gases contg. it under temp. conditions which are controlled so as to avoid polymerization, i. e., at temps. below 30° or above 100° , for instance, 130 – 150° . A suitable construction is specified.

Hydrochloric acid. W. SCHWARZENAUER. Ger. 279,008, Oct. 3, 1914. A vertical retort is used in decomposing $MgCl_2$ with superheated steam. The steam is admitted at the upper end of the reaction chamber.

Hydrochloric acid. E. TEISLER. Ger. 300,723, Oct. 4, 1919. To a mixt. of $NaHSO_4$ and $NaCl$ which is to react in the presence of heat, is added some solid material which is attacked by neither HCl nor H_2SO_4 , e. g., a metal sulfate, or C in the form of graphite, retort carbon, anthracite, or soot.

Hydrochloric acid from chlorine and hydrogen in gaseous form. C. W. BAUMANN. Ger. 301,903, Nov. 10, 1917. Cl produced from the electrolysis of $NaCl$ or $MgCl_2$ is mixed with H shortly before their combustion in the suction chamber of a 4-cycle internal-combustion engine, subjected to compression and explosion; HCl is driven out on the exhaust stroke. The gas is absorbed in vessels contg. H_2O in the usual manner.

Hydrochloric acid from chlorine and hydrogen in gaseous form. C. W. BAUMANN. Ger. 305,306, April 23, 1918. Addition to 301,903 (cf. above). To avoid overheating the engine in which, according to the main patent a mixt. of Cl and H are burned, 30–50% of HCl gas is added to the mixt. Air is not suitable since it induces rapid oxidation of the engine.

Ferric oxide; hydrochloric acid. D. TYRER. Brit. 183,323, June 8, 1921. Fe_2O_3 suitable for use as a pigment is obtained by heating $FeCl_3$ in a current of air and steam. The $FeCl_3$, preferably in the granular form obtained by evap. pickle liquor with stirring, is spread on the floor of a muffle furnace and air moistened by passing through H_2O at 60° is heated to 250 – 300° and passed over it. The exit gas is cooled to obtain HCl , and the rate at which the current is passed should be such that the acid condensed contains not more than 30 g. HCl per 100 cc. The gases leaving the condenser are passed to a scrubber fed with H_2O or pickle liquor. Fe compds. decomposable under the conditions of the process, such as hydrated Fe_2O_3 or $FeCO_3$, may be mixed in finely divided form with the $FeCl_3$, and in that case the temp. may be carried higher, for instance to 350° . There may also be added to the $FeCl_3$ small quantities of salts having a catalytic effect, namely salts of Cu , Mg , Sn , Na , and K . The addition of a Cu salt improves the red color of the product.

Hydrochloric or hydrobromic acid from free chlorine or bromine. CONSOLIDIERTE ALKALIWERKE IN WESTEREGGELN. Ger. 318,875, July 21, 1919. Brown coal is placed in an oven similar to a shaft oven made of masonry, the bottom of which is in the form of an inverted cone and contains the door from which the coal is removed from the oven. Unheated Cl or Br gas is introduced into the oven near the lower end and passes through the charge of coal; the resulting HCl or HBr is collected from an outlet near the top of the oven.

Producing hydrochloric acid and magnesia by heating magnesium chloride or magnesium oxychloride. P. BECK. Ger. 304,342, Dec. 24, 1919. Solid $MgCl_2$ or $MgO \cdot MgCl_2$ is mixed with a small amt., e. g., 2-5%, of $MgSO_4$ in aq. soln. The mixt. is molded and dried and subjected to the known heating with H_2O or steam.

Ammonia. L. CASALE and R. LEPRESTRE. Brit. 185,179, May 24, 1921. An app. for the catalytic synthesis of NH_3 is constructed of three concentric tubes, the outer being the pressure tube, the middle one contg. the catalyst and the inner one provided with a heating element. The entering gases pass first between the outer and middle tubes, then traverse the inner tube and are finally conducted through the contact material. By this means, the internal wall of the pressure tube is protected against excessive heating.

Alkali sulfides and hydrosulfides. J. EPHRAIM. Brit. 184,795, Aug. 12, 1922. Alkali sulfides and hydrosulfides are obtained by causing H_2S to react upon alkali salts such as sulfates or carbonates in presence of an alk. earth (including Mg) oxide or hydroxide; alk. earth compds. are employed which yield an insol. compd. as by-product.

Grading alkaline earth carbonates. W. W. FLOWMAN and W. FELDENHEIMER. Brit. 183,243, April 19, 1921. Alk. earth carbonates are graded by treatment in finely powdered form with a dil. aq. soln. of an alkali silicate. The quantity of silicate required depends, to some extent, on the hardness of the H_2O used, but is generally of the order of 0.5-1.5% of the wt. of the carbonate. A higher concn. is desirable for $MgCO_3$. The carbonate is conveniently treated in the form of a 5-10% mixt. with H_2O ; under the action of the silicate the coarser material ppts. and may be sep'd., after which the alk. earth carbonate is recovered from the suspension in a very finely divided form. As flocculating agent for the very fine suspension a soln. of gelatin or glue may replace alum or $Al_2(SO_4)_3$, and the flocculation process may be performed gradually, so that the sedimentation of the flocculated carbonate is retarded. Cf. 2379, 1911 (C. A. 6, 1964) and 27,930, 1911 (C. A. 7, 1846).

Sodium hydroxide. COURTAULDS, LTD. and R. O. JONES. Brit. 182,411, June 11, 1921. Na_2CO_3 is removed from solns. of NaOH such as solns. produced by the two-stage caustifying process described in 182,661 (C. A. 16, 4303) by adding excess of $CaCO_3$ and if desired seeding with $CaCO_3 \cdot Na_2CO_3$. A ppt. of $CaCO_3 \cdot Na_2CO_3$ is produced, from which the Na_2CO_3 may be recovered by treatment with H_2O . The remaining Na_2CO_3 may be removed by concentrating the soln. to a strength of 30-35% and cooling to 10-20° when small crystals of Na_2CO_3 sep., or by treating with the necessary quantity of SiO_2 or BaO . The soln. thus further purified contains less than 1% of Na_2CO_3 .

Sodium, potassium and ammonium phosphates. J. G. WILLIAMS. Brit. 184,206, Nov. 10, 1921. Mineral or pptd. $Ca_3(PO_4)_2$ or bone ash is mixed with a soln. of Na, K, or NH_4 sulfate and the product treated with SO_2 . The reaction products are $CaSO_4$ and a sol. phosphate corresponding to the sulfate used, a sol. sulfite being also formed. The formation of sulfite can be avoided if one of the three mols. of sulfate required for the reaction is replaced by one of H_2SO_4 , and this may be accomplished, with Na_2PO_4 , by the use of niter cake. No sulfite is formed when pptd. $CaHPO_4$ is treated, and in this case the SO_2 can be recovered by heating the filtered reaction liquid. Other acids readily volatile from hot solns., such as $HOAc$ or formic acid, or CO_2 , or H_2S , may replace SO_2 . Cf. 26,097, 1912 (C. A. 8, 1648).

Chlorates; hypochlorites. M. WILDERMAN. Brit. 183,671, June 16, 1921. Chlorates and hypochlorites of Ca or Mg are manuf. by chlorination of the corresponding hydroxide, and KClO_3 is prepd. therefrom. A dil. suspension of the hydroxide is chlorinated, and fresh material is added from time to time, until a soln. of chlorinated products of 60–64° Tw. is obtained. A distributing plate together with ebonite-coated glass balls serves to distribute the liquor and expose a very large surface to the action of the Cl, while at the same time preventing the deposition of solid matter in the towers. The temp. during chlorination is kept below 70° by using dild. Cl, and, if necessary, by adding H_2O to the liquor in the mixer. To prep. KClO_3 , KCl in an excess of 2% over the theoretical amt. is added, and the bulk of the chlorate allowed to crystallize at atm. temp. The mother liquor is dild., if necessary, until there is present preferably 45–50 g. CaCl_2 in 100 g. of H_2O , when the liquor may be cooled to -20° to sep. further quantities of KClO_3 , without simultaneous sepn. of ice or CaCl_2 . A suitable construction is specified. Cf. 20,068, 1886, 13,263, 1908, and 12,424, 1909.

Chlorine or sulfuryl chloride and sulfates. F. BERGRUS. Ger. 299,034, Aug. 23, 1919. A rotary oven which is placed obliquely, is used charged with finely pulverized NaCl. The gas given off from a pyrite roasting oven, mixed with air or O, is introduced into the lower end of the rotary oven. The reaction temp. is above 500° but lower than the m. p. of any chloride-sulfate mixt. that may be present during the process. Fresh salt may be introduced into the upper end of the oven and the decomposed salt removed from the lower end without interrupting the reaction process, which may thus be made continuous.

Crystallizing copper sulfate. J. M. DOSSETT. Brit. 184,527, March 31, 1921. CuSO_4 liquor is rapidly cooled in a smooth vessel with continual agitation by means of an air blast or mechanical stirrer. A suitable construction is specified.

Purifying mineral substances. A. L. A. TEILLARD. Brit. 183,443, July 6, 1922. Mineral substances, particularly BaSO_4 , are purified by heating the broken material in a furnace to about 300° and then sepg. the portions that have become reduced to powder by the heating from the portions that have remained unchanged.

Utilizing the waste magnesium chloride lye from the potash industry. CHEMISCHE FABRIK BUCKAU. Ger. 283,096, March 30, 1915. The lye, to which H_2SO_4 has been added, is heated to about 120°, and the HCl thereby formed is collected in the usual manner. MgSO_4 is evapd. from the soln. remaining.

Utilizing the waste magnesium chloride lye from the potash industry. CHEMISCHE FABRIK BUCKAU. Ger. 284,177. Addition to 283,096 (cf. above). May 10, 1915. The process according to the original patent is conducted under vacuum.

Utilizing the waste magnesium chloride lye from the potash industry. CHEMISCHE FABRIK BUCKAU. Ger. 290,876, Mar. 23, 1916. Addition to 283,096. The decompn. of the MgCl_2 is effected by a mixt. of SO_2 , *e. g.*, that coming from the roasting of pyrites and O (as found in air) in the presence of H_2O in the form of steam.

Separation of phosphorus from acetylene. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE GES. Brit. 184,184, Aug. 1, 1922. P compds. in C_2H_2 are oxidized to P and removed as such by treatment with O, preferably at a raised temp., in the presence of activated charcoal as catalyst. C_2H_2 mixed with a small proportion of O, air, etc. is passed through a reaction tower packed with activated charcoal and heated to 80–100°; alternatively, C_2H_2 and air, etc. are passed in succession over the charcoal. P is recovered by extg. the charcoal with hot H_2O .

Hydrogen peroxide. CHEMISCHE FABRIK WEISSENSTEIN GES. Brit. 184,153, June 23, 1922. Vessels used in the prepn., distn., or concn. of H_2O_2 are made of tantalum.

Oxygenated water. AQUAZONE LABORATORIES, INC. Brit. 185,659, Oct. 13,

1921. Supersatd. solns. of O contg. more than 35 cc. of gas per l. are obtained by treating H_2O with a continuous stream of atm. air, preferably in jet form, the temp. being maintained below $60^\circ F.$ and the pressure at about 10 atms.

Titanium oxide. G. CARTERET and M. DEVAUX. Brit. 184,132, June 27, 1921. Residual acid is eliminated from TiO_2 by treatment with an alk-earth chloride soln. The oxide is then washed with milk of lime or baryta to remove the HCl produced, and is finally dried. Cf. following abstract.

Titanium oxide. G. CARTERET and M. DEVAUX. Brit. 185,374, June 27, 1921. Cryst. TiO_2 free from Fe is prepd. from the iron-free $TiCl_4$ obtained by the process described in 184,948. The chloride is dissolved in H_2O and the soln. neutralized to ppt. the hydrated or gelatinous oxide. This is dissolved in H_2SO_4 , preferably of 25% strength and the soln. boiled to ppt. the oxide. This pptn. is facilitated by slight hydrogenation, which may be effected either by direct addn. of the gas, or by addn. of Zn to the soln. The amorphous oxide pptd. is calcined to yield the cryst. oxide.

Lead oxides. SOC. GAMICHON FRÈRES. Brit. 184,798, Aug. 14, 1922. Pb oxides are produced by feeding solid, powd., or liquid Pb into one end of a horizontal rotary cylinder suitably heated and provided with baffles which retain the Pb in the app. for the necessary time. A current of air, which may be under pressure, passes through the app., and may carry an agent capable of facilitating the oxidation. The product is discharged at the outlet end into a hopper.

Compound for the sharpening of tools. A. N. J. ZIRSEN. Can. 225,244, Oct. 24, 1922. The compd. is prepd. by mixing fuming HNO_3 , 350, fuming H_2SO_4 , 450, and pure HNO_3 , 250 g., and dilg. the mixt. with H_2O .

Plastic compositions. G. BORLE. Brit. 184,167, July 19, 1922. Fibers are thoroughly impregnated and made into a pulp with H_2O or with Na_2SiO_3 soln., to which metallic oxides or salts may be added. Milk of lime, $Al_2(SO_4)_3$, or $MgCl_2$ soln. may be used in conjunction with the Na_2SiO_3 soln. to ppt. silicic acid on the fibers. The treated fibers are mixed with a filler such as sawdust, broken stones, asbestos dust, and with a binding means such as cement. Bitumin, tar, pitch, tar oil, resin soaps, etc. may be added for waterproofing, and coloring agents may be added. The mass may be made into plates, suitable for floorings, on a card-board machine. Instead of Na_2SiO_3 , a soln. obtained by partly decomposing hydrofluosilicic acid with a metallic oxide or carbonate, e. g., $MgCO_3$, may be used to impregnate the fibers.

Plastic compositions. G. C. DEVONSHIRE and E. T. FOORD. Brit. 184,563, May 12, 1921. A compn. for making buttons, insulators, and other articles, consists of 12 parts of ground bone, 3 parts of casein, and 2 parts of lime, with or without 1-2 parts of Na_2SiO_3 . Sufficient water is added to produce a plastic mass.

Gas-imperious materials. BRITISH THOMSON-HOUSYON CO., LTD. Brit. 184,012, June 30, 1921. Materials which remain pliable and impervious to gases at low temps. are obtained by impregnating an internal animal membrane with a mixt. contg. a hardening agent, such as nigrosine, and a hygroscopic polyhydric alc. having a low freezing point. The membrane, which is preferably obtained from the throat lining or the bladder of cattle, may before impregnation be treated with a dil. soln. of a vegetable tanning agent, such as gallic or tannic acid. A suitable impregnating agent consists of glycerol 30 parts, ethylene glycol 5.5 parts, nigrosine 2 parts, and H_2O 70 parts.

Phenol-aldehyde condensation products. LORIVAL MANUFACTURING CO., LTD. AND A. A. DRUMMOND. Brit. 184,961, July 1921. A synthetic resin is formed by adding a glycerol soln. of a mineral acid in a definite proportion to an initial phenol-aldehyde condensation product, the proportion being at least 900 g. of glycerol (or aq. glycerol contg. at least 70% of glycerol) to 1 g.-equiv. of acid. A bleaching agent may also be employed. In an example, hypophosphorus acid is used as bleaching agent and HCl

as the mineral acid. The material may be dissolved in alc. for use as a *varnish*, or may be hardened in molds for use as *elec. insulating material*.

Waterproofing. F. MOELLER. Brit. 184,462, Aug. 1, 1922. Cellulosic, etc., materials are waterproofed by treatment with thionyl chloride or S chloride or dichloride in the atomized state. The liquid may be sprayed in a chamber by a sprayer and thence carried by a pipe to the treating chamber through which the material such as paper is passed. The circulating system contains a drying app. for sepg. H_2SO_4 and HCl, and a blower. The material may alternatively be passed over a porous block satd. with the reagent; or the latter may be applied by porous rollers dipping into the liquid or by rollers sprinkled with it.

Fire-extinguishing liquid. E. R. BRONYON. Can. 225,535, Oct. 31, 1922. A fire-extinguishing compd. contains $NaHCO_3$ and an albuminous substance and may contain Na_2CO_3 and an NH_4 salt which depresses the f. p. Cf. C. A. 16, 2534.

Casein. R. H. ABBEY. Brit. 183,972, May 30, 1921. Casein is prepd. for use as a plastic material by dissolving it in a soln. of Na or K carbonate, Na silicate, borax, or NH_4 , adding coloring matter to the soln., if desired, and pptg. the casein with the reagent described below. The ppt. is worked up by beat into the desired forms and hardened with HCHO. The pptg. agent is made by dissolving Zn sulfite, K or sodium meta-bisulfite, glacial HOAc, and alc. in H_2O , adding Zn cuttings, decanting the clear liquor, treating this with milk of lime, and filtering.

Utilizing rice waste. H. WIEDEMANN. Brit. 185,083, Dec. 22, 1921. The waste resulting from husking, shelling, and polishing rice is subjected to dry distn., if necessary under reduced pressure, and the distillate condensed and collected. The latter consists of a mixt. of paraffins, phenols, coumarone-like resins, and org. acids. The charcoal obtained is especially suitable for decolorizing and purifying purposes owing to its high content of silicic acid.

Röntgen-ray apparatus; catalytic agents. P. L. G. MARCOTTE. Brit. 184,485, Aug. 10, 1922. Crystals between certain narrow limits of size are refined by double sifting or other means. They are employed for fluorescent screens in X-ray work, or for use as catalytic agents in chem. reactions.

Treating blood. F. W. V. FITZGERALD. Brit. 183,943, May 5, 1921. The fluidity of blood is preserved or its coagulation retarded by the addn. to it while still liquid of a quantity of a neutral or alk. soln. of an oxalate or fluoride such as NH_4 oxalate or NaF . The means employed may be used separately or in combination, and if desired a preservative may be added. The application of the process in the production of a substitute for vulcanite, horn, or the like is mentioned.

Treating algae. SOC. MARITIME DE PRODUITS CHIMIQUES. Brit. 183,412, Sept. 15, 1921. Seaweed, etc., is incinerated at a moderate temp. under such conditions that a light finely divided ash is obtained. The ash is lixiviated while still hot. A suitable construction is specified.

19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

Glass manufacture in Burma. ANON. *London Times Trade Supplement* 11, 29(1922).—Burma possesses large quantities of raw materials. A native Burman has established a glass factory near Rangoon. O. P. R. OGILVIE

Ceramic art and decoration. G. FERRAND. *J. Am. Ceram. Soc.* 5, 743-57(1922).—The artistic phases of terra cotta use. C. H. KERR

The organization of a decorative ceramic research department. F. H. RHEAD. *J. Am. Ceram. Soc.* 5, 758-87(1922). C. H. KERR

Formation of clays. ANON. *Brick Pottery Trades J.* 30, 14(1922).—Properties of clays vary according to their origin. True kaolins are derived from feldspars whereas the clays derived from porphyry and basalt are different. Climatic conditions are also important. In tropical climates laterites are formed with a considerable amt. of Fe, but in milder climates clays contg. less Fe are formed, owing to the effect of humus on the formation of the clay, the proportion of humus being greatest in milder climates. The method of transportation whether by H₂O, ice or wind also exerts important influences. Fireclays although free from most of the fusible impurities often have nodules of FeS₂ which have been formed by the decompn. of vegetable matter in clay, and its action on the Fe compds. H. G. S.

The properties of some ball clays. H. H. SORRWELL. *N. J. Ceramist* 2, 5-15 (1922).—American clays contain less material coarser than 120-mesh than English clays. English clays vitrified at low temps. and remained almost const. in porosity and vol. to cone 12, without signs of overfiring. American clays showed gradual reduction in porosity from cone 01 to cone 12 and constantly changing vol. With 1 exception they did not vitrify before cone 12. Tenn. clays vitrified before Ky. clays. Comparisons of color were made on test pieces of a standard body mixture. American clays showed a good color. Tenn. clays were better than Ky. American clays nearly equal the English in plasticity. They require more exact firing because of the variations in porosity and vol. with slight changes in heat treatment, which is the reason for the difficulty observed in attempts to substitute American for English clays. The more porous body obtained by substitution of American clays is conducive to crazing. Successful substitution requires a little higher firing or readjustment of the flux content to produce the same degree of vitrification. C. W. PARMELEE

The dissociation of clay by lime. E. SELCH. *Speersaal* 55, 1, 2(1922).—The effect of CaO upon ceramic bodies was studied (*Speersaal* 1916, 173). After the bodies had been fired, the SiO₂ and Al₂O₃ sol. in HCl and NaOH were detd. At Cone 04a it is necessary to have 2 mols. of CaO to decompose 1 mol. of clay. After firing at cone 9 it is necessary to have only 1 mol. of CaO to decompose 1 mol. of clay. The above tests were continued more thoroughly. Different mixts. of CaO and clay were fired to different temps. and the percents sol. in HCl and NaOH were detd. The higher the CaO the more thoroughly was the clay decomposed after firing. A mixt. of 1 mol. clay and 2 mols. CaO is almost entirely sol. in HCl after firing to cone 1a. The CaO even when fired to a high temp. in a CaO-clay mixt. is almost entirely sol. in HCl. In some cases the mixts. become more sol. when fired to the higher temps. whereas in others they become less sol. H. G. SCHURECHT

Bauxite clay in Ayrshire. G. V. WILSON. *Memoir Geol. Survey Scotland* 1922.

O. P. R. OGLVIE

The reversible thermal expansion of silica. H. S. HOULDSWORTH and J. W. COBB. *Trans. Cer. Soc. (England)* 21, 227-76 (1921-2).—See C. A. 16, 805. E. J. C.

Investigation of dust press practice as influencing finished sizes and cracking. H. SPURRIER. *J. Am. Ceram. Soc.* 5, 798-805(1922).—The % H₂O is the dominant factor affecting shrinkage. Ordinary rate of pressing gave 3.42% porosity, a slower rate 0.66% and a still slower rate 0.37%. C. H. KERR

The effect of some fluxes on the absorption and transverse strength of a terra cotta body. E. C. HILL. *J. Am. Ceram. Soc.* 5, 832-6(1922).—Feldspar, in amts. of 5-10%, may be used. Albany slip clay is not good because it darkens the body and increases the drying shrinkage. Powd. glass is very good—probably the best flux. White lead is not good, also it is expensive. Cryolite is good, but too costly. Whiting and

fluorspar are not good. $MgCO_3$ is poor. Furnace slag may be good if sufficiently free from Fe.

C. H. KERR

The measurement of the plasticity of clay slips. R. E. WILSON AND F. P. HALL. *J. Ind. Eng. Chem.* 14, 1120-5(1922).—For casting consistency, plasticity should be expressed in terms of (a) H_2O content required to give good working consistency and (b) resistance to deformation by small loads. A modified Bingham plastometer was used in the tests. The % H_2O required varies greatly and bears no exact relationship to the usual classification as to plasticity. Small amts. of acid or alkali have little effect on the mobility of a clay slip but large effect on the yield value, the variations being greater than the difference between a nonplastic kaolin and a very plastic ball clay. The H-ion content of the slip H_2O must be controlled. The plastometer, properly standardized, may be very useful as a standard for ceramic testing. Also in *J. Am. Ceram. Soc.* 5, 916-27(1922).

C. H. KERR

Note on the cause of the "splitting" of a pottery body. M. B. CRAVEN. *J. Soc. Chem. Ind.* 41, 329-30T(1922).—In making ring supports for incandescent gas mantles trouble was encountered in splitting or splintering off. English bodies were compared with a satisfactory Germany product. Chem. analyses were about the same. The German rings showed no large content of MgO although they were sold under the name "Magnesia." Porosities were about the same—10-13%. Sections examd. under a magnification $\times 30$ showed the marked superiority of the German ware, fine grained, homogeneous and free from laminations or cracks, in contrast with irregular grains, imperfect cohesion and striations in the English rings. The German body analyzed SiO_2 66.25, Al_2O_3 31.93, Fe_2O_3 0.72, P_2O_5 1.03, CaO 0.03, MgO 0.70, ign. loss 0.22%. alk. very low.

C. H. KERR

Keeping water out of the clay pit. ANON. *Brick Pottery Trades J.* 30, 16(1922).

H. G. SCHURECHT

Lime bricks. ANON. *Raw Materials Review* 1, 83(1922).—Servange, of France, claims to have produced CaO -bricks from raw chalk of limestone waste and clay or sand, by mixing sand or clay in any proportion with chalk and pressing the product wet. The bricks are heated to 500-550° for a few hrs. The atm. in the kiln is kept moist by forcing steam into it, in order to obviate the complete dessication of the bricks. The too rapid escape of the CO_2 must be prevented by the use of proper dampers, as its presence is indispensable for hardening.

O. P. R. OENLIVIE

Note on ladle brick. D. A. MOULTON. *J. Am. Ceram. Soc.* 5, 823-5(1922).—The best ladle bricks have a fusion point of cone 26, give 15 to 20 beats and are made without addn. of any sandy material. Ordinary tests for refractories are too severe and should be modified.

C. H. KERR

Carbon Brick. A. P. *Deut. Töp. Ziegler Ztg.* 53, 219-20(1922).—The advantages of C brick for refractories are their resistance to high temps., to sudden temp. changes and to slag action. In their manuf. hard coke contg. not over 8% ash is employed. It is crushed to 2 mm. size and mixed with 20% hot tar. The batch is thoroughly pugged and the bricks are molded in wooden molds. They are dried for 2-3 weeks and fired. In firing they are packed in powd. coke in a sagger or partition in a kiln and fired at cone 12. Slow cooling seems necessary. Rapid cooling develops cracks. In laying C brick a mortar contg. 20% clay and 80% coke dust is used. According to Seiger (*Stahl u. Eisen* 41, 1912) C brick are best suited for lining blast furnaces producing high-C gray Fe. Their value for metallurgical furnaces has not been thoroughly investigated.

H. G. SCHURECHT

Coal saving methods in brickworks. ANON. *Brit. Clayworker* 30, 231(1922).—The following figures show the relation between the % CO_2 and fuel wasted, resp: 5, 7, 9, 11, 13, 14%; 50, 35, 27, 23, 21, 20%.

H. G. SCHURECHT

Effectiveness of different methods of making absorption determinations as applied to hollow building tile. H. D. FOSTER. *J. Am. Ceram. Soc.* 5, 783-97(1922).—Specimens from 17 different sources were tested by (1) immersion in H_2O at room temp. for various times from 15 min. to 9 days, (2) boiling for 1 to 5 hrs., then cooling for at least 1 hr., (3) repeated vacuum treatments. Cold H_2O immersion gave 73.5%, boiling treatment 92.7% and vacuum treatment 97% satn. Boiling for 5 hrs. gave results 1.2 times the value for 72 hr. immersion in cold H_2O in the case of shale tile, 1.35 for fireclay tile, 1.20 for surface clay tile, 1.25 for mixed clay tile and 1.28 av. for all tile. The best practical test is to boil for 5 hrs., then cool at least 1 hr. before the satd. wt. is taken.

C. H. KERR

Ball and pebble milling for pulverizing and mixing (pottery materials). H. J. KLINFELDT. *N. J. Ceramist* 1, 164(1921).

C. W. PARMELEE

Importance of grinding (pottery materials). HARRY G. WOLFE. *N. J. Ceramist* 1, 167(1921).

C. W. PARMELEE

Some new forms of kilns. A. DUCKHAM. *Engineering* 114, 534-6(1922).—Two kilns, one continuous, the other tunnel, are described. The continuous kiln has 16 chambers each 19 ft. wide, 17 ft. long, 6 ft. high at the sides and 10 ft. at the middle. The chambers are in 2 rows of 8 each. There are 4 fireboxes, 2 on each side of each chamber. Firebricks are burned to cone 13. Fuel consumption is 20-25 tons of coal per 100 tons of brick. Air leakage, chiefly through the main dampers to the chambers, interfered with draft and cast iron flap doors were put in. Artificial draft also was introduced. A new modification with central bags feeding producer gas is described. The tunnel kiln described has a fixed central heating zone and the hot gases follow a zig-zag path. A modification in annular form was devised for burning glazed ware. Excellent drawings are given.

C. H. KERR

The use of hot air in continuous kilns. ANON. *Brick Pottery Trades J.* 30, 10-11 (1922).

H. G. SCHURECHT

Pot bank firing with petroleum residues. M. A. GRANGER. *Oil Eng. Finance* 2, 477(1922).—Expts. with a special pottery kiln designed to burn petroleum residues are described. An oxidizing atm. must be maintained and the flame must not be of too high temp. so as to cause over-burning and local fusion. The firings were satisfactory, regulation was easy and the expense equiv. to that of a wood-fired kiln.

D. F. B.

Standardization of refractories. R. C. PURDY. *Chem. Met. Eng.* 27, 637-8 (1922).—Present knowledge does not allow the writing of satisfactory specifications for refractories. General classification of each type into "heavy," "medium" and "light duty" will not answer for all industrial purposes. Committee C-8 of Am. Soc. Testing Materials will prep. "suitability" and "control" tests for each industrial case.

R. J. MONTGOMERY

Properties of refractories under load at high temperatures. E. L. DUPUY. *Ceramique* 25, 308-310(1922).—The strength at high temps. was measured by means of impact, by increasing the load from zero at a rate of 150 kg. per min. and by means of a static load. The effect of firing temps. on a clay under load was also studied. It was found that the clay had max. strength at 1000° when fired to 1350° previous to testing and at 1150° when fired at 1500° before testing. The clay contained Al_2O_3 20.0, SiO_2 (free) 45.8, SiO_2 (combined) 26.9, Fe_2O_3 2.1, K_2O 0.51, Na_2O 0.11 and ign. loss 6.95%. The results of the tests with different loading methods indicate that the values obtained by impact and by increasing the load from zero are about the same and that these values are about $4\frac{1}{2}$ times those obtained with a static load.

H. G. SCHURECHT

Recent developments in refractories. W. F. ROCHOW. *N. J. Ceramist* 1, 181 (1921).—A general review.

C. W. PARMELEE

Electrical resistivity at high temperatures. M. L. HARTMANN, A. B. SULLIVAN

AND D. E. ALLEN. *Brick Pottery Trades J.* 30, 16(1922).—The elec. resistivity of 9 com. materials was detd. on $2\frac{1}{8}$ " cubes at 100° intervals up to 1500°. Fireclay bricks of "A" quality and coarse texture, hauxite bricks and SiO₂ bricks with CaO bond gave regular resistivity curves. SiC bricks contg. 95% carbofrax C and 5% bond gave similar curves, the resistivity being const. when the bricks were maintained at 1500°. Carbofrax B, on the contrary, showed a rapid decrease in resistivity with increasing time of heating. Recrystd. SiC ("Refrax") has quite regular curves, the resistivity being low at all temps. The resistivity curves of MgO bricks for heating and cooling are quite different in shape, and this difference, with a peculiar flattening of the heating curves (indicating a constancy of resistance) between 1000° and 1500°, appears to indicate that a phys. change of the structure occurs when MgO is heated. The difference between the heating and cooling resistivity of brick made from natural zirconia is very marked. On heating the resistivity fell very rapidly until a temp. of 1200° was reached, after which it fell very slowly indicating a permanent change on heating zirconia to 1200°. Coarse grained chrome bricks possess low resistivities at all temps, the resistivity remaining practically const. from 1100-1200°, increasing from 1200-1300° and again decreasing from 1300-1500°.

H. G. SCHURECHT

The use of pulsichrome from a manufacturer's stand point. F. CLARK. *J. Am. Ceram. Soc.* 5, 826-7(1922).—Spraying by the pulsichrometer has proven very successful. Pulsichrometer vs. old method of applying glazes. L. W. MUNSHAW. *Ibid* 827-31.—Duplication of colors is far easier with the pulsichrometer. C. H. KERR

"Blind" glazes. ANON. *Brick Pottery Trades J.* 30, 15(1922).—"Blind" glazes are those with dullness irregularly distributed over the ware so as to prevent their being passed as mat glazes. It is due to improper treatment at the close of firing. It is very liable to occur with high ZnO or CaO together with a small amt. of Al₂O₃, and when the kiln is soaked too long at the highest temp. To prevent it, add clay to the glaze and cool more rapidly. Since crystals do not readily form in a very fluid glaze, "hinding" may be overcome sometimes by finishing the fire about 1 cone higher. When Ph glazes are used, undue soaking periods at the high temps. are certain to cause hinding. Firing with a reducing kiln atm. or with a wet fuel will also cause this defect. H. G. S.

The furnace gas producer. C. W. PARKS. *N. J. Ceramist* 2, 46-56(1922).—The furnace gas producer is a simple, iron casting fitted to each fire box, thus changing each box into a producer. Steam is used. It is very economical and particularly good for salt glazing.

C. W. PARMELER

The effect of sources of pig iron upon the enameling of cast iron. M. E. MANSON. *J. Am. Ceram. Soc.* 5, 806-10(1922).—Cast Fe made from "northern" pig Fe blistered badly while that made under the same conditions from "southern" pig Fe was O. K. In castings from "northern" iron the content of combined C was low; otherwise they were about the same. Reducing Si in the castings from "northern" iron from 2.80 to 2.30%, with total C = 3.30%, eliminated blistering. Apparently cast Fe of this type with combined C less than 0.15% will cause blistering, but it is not yet positive that it is the combined C itself that is important. All blistering irons examd. showed characteristic dark blotches in the micrographs. These have not yet been identified.

C. H. KERR

The relative merit of heat-resisting alloys for enamel burning racks. E. P. POSTS. *J. Am. Ceram. Soc.* 5, 811-6(1922).—Racks fail by oxidation and warpage. Calite, hardite, nichrome, Ni and rezistal showed good heat resistance, thermalloy and misco fair, and monel, cast steel, calorized steel, steel and cast Fe poor. Cast steel resists oxidation considerably better than steel and some better than cast Fe. Only thermalloy, hardite, nichrome, rezistal and calite are highly resistant to oxidation. Addresses of the mfrs. of the special alloys are given.

C. H. KERR

Glass molds. R. L. FRINK. Brit. 183,582, April 26, 1921. Metal molds for glass working are made with a porous or finely pitted surface. Such molds may be made from an alloy of Al or Cu with Cu, Ba, or Mg, the surface being rendered porous by treating it with an alk. soln. A suitable alloy contains about 2% of Ca or Ba. In making such an alloy, it is recommended that an alloy contg. 75% of Al and 25% of Ca, etc., be first prepd. at a temp. of 500-1100°, and that this be added in the required proportion to pure molten Al. For use the molds may be dipped in H₂O, paraffin oil, etc.

Ceramic products. LAVA CRUCIBLE CO. OF PITTSBURGH. Brit. 185,435, March 8, 1921. Materials for making ceramic products contg. clay as a base are mixed with a metal or alloy in a finely divided state, to enable them to be dried quickly before fired. Al or Mg or alloys or mixts. thereof, or Zn or alloys thereof may be used. The clay may be mixed with sand, graphite, SiC, lime, magnesia, bauxite, or zirconia, for making refractory articles such as crucibles or pots. A glazed product may be obtained by incorporating with the mixt. another non-ferrous metal such as Cu, Ni, monel metal, Cr, or Co, in a finely divided state.

Treating clay. W. FELDENHEIMER and W. W. FLOWMAN. Brit. 184,271, May 9, 1921. A process for the treatment of clay comprises deflocculation of the clay in an aq. medium by means of a dil. soln. of HPO₃ or the metaphosphate of an alkali either alone or in conjunction with an alkali such as Na₂CO₃. The proportion of deflocculator may be varied according to the hardness of the H₂O used. The clay may be subsequently recovered from its suspension in any desired manner. When flocculation is adopted an aq. soln. of alum, or NaHCO₃ may be used as a flocculator, in the manner described in 121,191 (C. A. 13, 647). Cf. C. A. 16, 2206.

Refining clay. PLAUSON'S (PARENT CO.), LTD. Brit. 184,880, May 21, 1921. Pure kaolin is prepd. by sepn. of SiO₂ and other silicates by intensive mechanical disintegration at a peripheral speed of over 1000 m. per min., preferably in the colloid mill described in 155,836, with H₂O and with or without a dispersator, the kaolin being selectively colloidalized. Suitable dispersators are water-glass, tanning agents, humus and humic acids or their compds., saponin and other soap-like froth-forming substances or sol. silicates, aluminates, ferrocyanides, thiocyanates and borates. The resulting dispersion may be concd. by ultra-filter presses. The colloidal clay may be used in the manuf. of colloidal inks, as a filler in rubber mixings, etc. Cf. 3592, 1880.

Drying clay. T. RIGNY. Brit. 183,535, April 16, 1921. Pastes of china or like clay such as are dug from the ordinary settling pits are dried by being spread as films upon heated surfaces in app. such as that described in 149,055, in which the surfaces are heated by the vapors evolved from the film, after compression, or in the multiple-effect app. described in 180,963, and 181,035. A suitable construction is specified.

Porcelain. BRITISH-HOUSTON CO., LTD. Brit. 184,090, Sept. 27, 1921. A ceramic material particularly suitable for elec. insulation is obtained by firing a mixt. contg. 5-35% of beryl in addition to the usual ingredients, such as clay, silica, and feldspar.

Furnace for the melting of basalt. P. DRY. Can. 224,873, Oct. 17, 1922. A furnace has a shaft for feeding the charge to a reverberatory furnace having an inclined bottom, at the lower end of which is a basin from which the melted charge flows into fore-hearth at the sides of the furnace.

Abrasives. W. G. W. SANDISON. Brit. 185,578, July 16, 1921. Hydrated Mg silicates of the serpentine type contg. 3-5% of Fe are calcined at a bright red or white heat and ground for use as an abrasive or polish. Cf. 2321, 1883.

Refractories. DENIS LOUIS. Can. 225,725, Nov. 7, 1922. A porous refractory material contains 30 parts of pure rich refractory earth contg. 70-80% sand, 30 parts MgO, 25 parts light earth contg. 80% sand and 5 parts sawdust.

Refractory composition. C. A. WHITE. Can. 225,123, Oct. 24, 1922. A non-recrystd. refractory material contains SiC, cryst. graphite and a carbonizing binder. A flux such as borax or sand and borax may be used to form a protective coating around the particles of the composition.

Refractory composition. C. A. WHITE. Can. 225,124, Oct. 24, 1922. A refractory material contains a chemically inert refractory material, cryst. graphite and a carbonizing binder such as tar or pitch. A flux such as borax or sand and borax may also be used to form a protective coating for the particles of the material.

20—CEMENT AND OTHER BUILDING MATERIALS

C. N. WILEY

A study of conditions causing disintegration of cement under the "accelerated" test. A. G. FLEMING. *J. Soc. Chem. Ind.* 41, 300-2T(1922).—That the accelerated steam test on cement is unnecessarily severe and does not always indicate the quality of the cement has led to these conclusions from a series of expts.: (a) The chem. compn. of an av. port. cement gives little guidance as to its possible behavior under the accelerated test. (b) Unsound cement stored under water shows a marked improvement compared with that stored in air, either dry or moist; the natural storage for cement, at any rate during hardening, is under water. (c) Mortars poor in unsound cement improve more rapidly than mortars rich in unsound cement. There is thus little danger of disintegration of a water-stored concrete made from what are ordinarily termed "poor" cements. (d) Mortars in practice do not exhibit the weakness of their neat cement. (e) Mortars and concretes are improved by water-storage; concrete should be kept moist, at any rate until completely set. The disruptive force exhibited in the accelerated test is due principally to the free lime incorporated in the clinker particles and this force is not discovered except by rapid hydration. That the combination of the alkali bases with CO_2 from the air and S from the sulfides of the clinker may be also responsible for unsoundness is indicated from the expts. Fine grinding of raw mix to insure more intimate combination of the elements has eliminated much of the danger of unsoundness.

C. N. WILEY

Electric cement. ANON. *Rev. ing. index tech.* 29, 155-7, 197-8(1921); *France-Belgique* 1, 71-2, 199-200(1922).—"Electric cement" is an aluminous cement manufd. in the elec. furnace. The essential component is $\text{Al}_2\text{O}_3 \cdot \text{CaO}$ or the eutectic $3\text{Al}_2\text{O}_3 \cdot 5\text{CaO}$. The hydraulic index is generally above 1. The apparent d., with a degree of fineness such that 5% remains on a sieve of 4,900 meshes per cm^2 , is not over 1. When tested hot with LeChatelier cylinders it does not swell, and its contraction on setting is the same as that of ordinary cement. It is not decomposed by the sulfates of the alkalis or alk. earths or by sea-water; it hardens rapidly; with 300 kg. of cement to 1 m.³ of sand, the strength after 48 hrs. is more than double that of a similar mixt. of artificial portland cement after 90 days.

A. P.-C.

The caustic calcination of dolomite and its use in sorrel cements. G. A. BOLLE AND J. B. SHAW. *J. Am. Ceram. Soc.* 5, 817-22(1922).—Large-scale expts. are described. Two types of retorts were used in the calcining, wrought Fe and fireclay. By controlling the CO_2 pressure, less than 0.5% CaO was liberated. Apparently some dolomites are solid solns., others are double salts and still others are a mixt. of both types. The best temp. for calcining ore to be used in a sorrel cement is $725-50^\circ$. High- SiO_2 ores are inferior.

C. H. KERR

Artificial stone with asphaltic properties. *Raw Materials Review* 1, 180(1922).—The process was invented by Albert Flexer, of Vienna. The pitch residue from wood-tar, serves as the raw material, when the wood-tar, after oxidation is treated with a concd.

soln. of caustic alkali, and is then digested with dil. NH_4OH , alc., or like thinning medium. After skimming off the fluid resinous acids, the pressed cakes are heated with 5 to 10 times the vol. of H_2O to b. p., and then allowed to cool. The remaining wash-water is poured off, and the brittle cakes are freed from H_2O by pressure. The mass is melted and mixed with 4 to 5 times the amt. of sand or gravel, and formed into bricks, etc.

O. P. R. OGILVIE

New system of concrete construction. ANON. *Can. Eng.* 43, 413(1922).—The outer walls are clinker concrete slabs, $2\frac{1}{4}$ in. thick, faced with $\frac{1}{4}$ -in. cement mortar, a $4\frac{1}{2}$ -in. space being left, while the inner slabs are made of coke breeze and cement, also $2\frac{1}{4}$ in. thick.

O. P. R. OGILVIE

Effects of alkali on concrete in prairie provinces of Canada. T. THORVALDSON.

Contract Record (Canada) 36, 953(1922).

O. P. R. OGILVIE

Gypsum withstands fire. *Contract Record (Canada)* 36, 961(1922).—A building made with gypsum hoard on wood studding stood a severe fire test.

O. P. R. OGILVIE

Fuel and cement kilns. *London Times Trade Supplement* 11, 19(1922).—The use of rotary kilns in England shows a saving of 4-5% in coal and an increase of 10% in output.

O. P. R. OGILVIE

Thermochemistry of vertical (cement) kilns. J. B. *Rev. mat. constr. trav. pub.* 156, 169-72(1922).—In burning, the following reactions take place, (a) fuel is burned to CO_2 , H_2O and SO_2 ; (b) CaCO_3 and MgCO_3 are decompd. to their oxides and CO_2 ; (c) in some calcareous materials org. matter and S burn; (d) CaO reacts with SiO_2 and Al_2O_3 , the mass undergoing incipient fusion. Reactions (a) and (c) produce heat, and (b) absorbs heat. Berthelot and Le Chatelier maintain that (d) is exothermic, while Timm states that it is slightly endothermic, and Stanger and Blount that the evolution of heat is practically negligible. A heat balance is given accounting for all the heat put into the furnace.

LOUIS NAVIAS

Anhydrite as building material. *Raw Materials Review* 1, 180(1922).—The large beds of anhydrite in the Hartz could be utilized by grinding the decomposed product with 3.5% CaO . The result would be a building material suitable for walls, ceilings, floors, artificial stone, etc.

O. P. R. OGILVIE

Burlington creosotes cypress piles. G. A. HAGGANDER. *Ry. Main. Engr.* 18, 308(1922).—White cypress with considerable sap wood is being treated and used successfully. The treatment consists of steaming 2 hrs. at 20 lbs. pressure; 4 hrs. under 24-in. vacuum; soln. pressure max. 175 lbs. for 11 hrs. 20 min.; resulting absorption 23.01 lbs. oil per cu. ft.

R. C. BARDWELL

Wood preservation statistics for 1921. ANON. *Ry. Main. Engr.* 18, 310(1922).—Table is given showing total material treated by years since 1909 with amts. of creosote and ZnCl_2 used.

R. C. BAROWELL

Solidifying fibrous pulp (Brit. pat. 185,399) 23.

Floor coverings. C. R. LEECH. Brit. 184,953, June 30, 1921. The process of making a floor covering by satg. paper felt with a mixt. of pitch, flux oil, and bitumen, described in 164,092, is modified by the omission of the pitch and flux oil. Soft asphalt may be used instead of bitumen.

Floor and wall coverings. J. FRANKFURTER and E. A. JANSEN. Brit. 183,753, Oct. 10, 1921. Jointless floor and wall coverings are composed of a plastic compn. consisting of finely ground arenaceous quartz, ZnO , wood shavings, and K silicate soln.

Slabs, tiles, etc. DURATO ASBESTOS FLOORING CO., LTD. AND A. Z. NEMETH. Brit. 184,910, May 31, 1921. Sawdust is soaked in MgCl_2 soln. of 10°Bé until thor-

oughly satd. and then mixed with calcined magnesite, soap-stone, and a further quantity of $MgCl_2$ soln. of 15° Bé and molded into slabs or tiles. The proportion of magnesite to sawdust is 1:3:4 by vol., and the soapstone may be $1/10$ of the combined sawdust and magnesite. After molding, the slabs are coated with a waterproofing compn. The articles may be reinforced.

Bituminous compositions for roads, etc. A. R. TABARY. Brit. 183,914, April 28, 1921. A mixt. of coal-tar pitch or resin pitch, clay, limestone, and asphalt is combined with an aggregate consisting of fine sand or of crushed or powdered hard materials, such as porphyrite, trap, quartzite, or slag. The proportion of clay should be from $1/2$ to $2/3$ of the quantity of pitch, and that of limestone from $3/4$ to an equal quantity of the amt. of pitch. The amts. of asphalt and of aggregate should each be equal to the combined wt. of the pitch, clay, and limestone. Bitumen, sawdust, destructor residues, or cement may also be incorporated in the mixt. The compn. may be used either as a road-making material in conjunction with stones and tar, bitumen, oils, etc. as a surface dressing with or without an admixt. of tar, or as a cement for filling the joints of stone or wood paving. It may also be compressed into paving slabs or tiles.

21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

Patent fuel. III. Research on the manufacture of briquets. ARTHUR GROUNDS. *Fuel* 124, 174-7(1922); cf. *Fuel* 124, 119-22; 144-51.—Problems in briquet manuf. awaiting soln. are enumerated, and both lab. and large-scale research are suggested.

C. C. DAVIS

Fuel oil problems of the Pacific ocean. C. E. KERN. *Oil and Gas J.* 21, No. 22, 80, 86(1922).—Statistics of resources are given.

D. F. BROWN

Utilization of vegetable oils as motor fuels. MATHOT. *Bull. mat. grasses inst. colonial Marseille* 1921, 116-28 pp.—Palm oil, cottonseed oil, and heavy petroleum were used as fuels in semi-Diesel engines of five different makes. A thermal efficiency of 24.5% corresponding to 278 g. of cottonseed oil per B.h.p.-hr. was obtained. Suggestions of changes in design necessary to adapt an engine to vegetable-oil fuels are given. The physical properties and ultimate analyses of palm, peanut, cottonseed, and sesame oils are reported.

E. H. LESLIE

Preparation of motor fuel from vegetable oils. A. MAILHE. *J. usines gaz.* 46, 289-92(1922).—M. explains how vegetable oils can be transformed easily by catalytic means into gaseous and liquid hydrocarbons with production of small amts. of CO_2 and CO. The gaseous products are essentially forms of H , CH_4 , C_2H_2 and C_2H_{10} and a small amt. of ethylenic hydrocarbons. Gas from peanut oil analyzed CO_2 6, CO 5, C_2H_2 6, C_2H_{10} 31, CH_4 38 and H 15%. The liquid products, after neutralization and hydrogenation, are made up of a mixt. of formenic and cyclic hydrocarbons, in which are found considerable proportions of benzene, toluene and *m*-xylene. They form a motor fuel with a very agreeable odor, similar to Borneo petroleum. J. L. W.

Progress in coal refining. A. SANDER. *Chem.-Ztg.* 46, 825-6, 874-6(1922).

E. H.

The preparation and economic use of coals, particularly lignites. K. KEGEL. *Naturwissenschaften* 10, 855-61, 882-8(1922).—A review and discussion including data for coal, coke and lignite.

C. C. DAVIS

The firing of powdered coal. RABU. *Bull. soc. ind. Nord France* 1921, no. 218; *Rev. universelle mines* 14, 68-70.—The prepn. of powdered coal by various methods, its uses, advantages, disadvantages and its future are discussed.

C. C. DAVIS

The oxidizability of coal and the determination of moisture. E. MERTENS. *Bull.*

fed. ind. chim. Belg. **1**, 361-4(1922); *J. Soc. Chem. Ind.* **41**, 577A.—Three g. of a sample of fat coal ground to 70 mesh were spread on the bottom of a dish 4 cm. in diam. which was suspended in a *drying oven* from the beam of a balance by a fine non-oxidizable metal wire. The wire passed through the top of the oven so that it was unnecessary to remove the sample to weigh it. The distance between the oven and the balance was sufficient to prevent any error due to heat. The sample lost 1% in wt. during the first 15 min. of drying at 105° but gained steadily thereafter because of *oxidation*. After 36 hrs. drying the sample had regained its original wt.; after 1400 hrs. it had gained 5.97%. *Distn. with xylene* gave approx. the same values as heating 15 min. at 105°. The former method, using a 50-g. sample of coal, is recommended. Wm. STRICKER

Low-temperature carbonization. S. W. PARR. *Gas Age-Record* **50**, 531-4(1922).—The fundamental principles of the Parr-Layng process of low-temp. carbonization by which non-coking, high-O coals can be successfully carbonized are explained. Two features are of fundamental importance. First, the control of the reactions during the coking process between the cellulosic and the bituminous substances of which the coal is composed, so that the deleterious effects of the high O compds. are neutralized without destroying the bonding property of the bituminous material. Second, the maintenance of low-temp. conditions throughout a large mass of coal, thus obviating the secondary decomps. which characterize the usual practice; this is accomplished by utilizing the exothermic reactions of the process, thus making an asset of the high O content, whereby the slow effect by cond. is replaced by the relatively quick procedure of autogenous chem. reaction throughout the mass. The results obtained are highly satisfactory. J. L. W.

Fifty years of development in the coke-oven industry. G. E. T. *Gas u. Wasser-fach* **65**, 436-8(1922).—A sketch of the life and work of Dr. C. Otto, and the development of the Otto-Hoffman and the Otto-Hilgenstock coke ovens. J. L. WILEY

Peat, history of its use. F. A. WILDES. *Proc. Minn. Surveyors and Engrs. Soc.* **26** and **27**, 114-22(1921-22).—A general paper, with special reference to Minnesota conditions. JACK J. HINMAN, JR.

The utilization of peat. F. A. WILDES. *Proc. Minn. Surveyors and Engrs. Soc.* **26** and **27**, 151-9(1921-22).—A review of the technical methods of converting peat into briquets and other useful forms of fuel. JACK J. HINMAN, JR.

The industrial exploitation of peat. M. TONNELLE. *Oil Eng. Finance* **2**, 482 (1922).—Treatment of the peat after the cutting, briquetting, use of peat in the fertilizer industry, distn. of peat, and details of the industry in North Germany are discussed. D. F. B.

The dispersoid chemistry of peat. III. Dehydration of peat at temperatures below 100°. W. O. OSTWALD AND A. WOLF. *Kolloid Z.* **31**, 197-200(1922).—Peat was heated to various temps. below 100°. Water was released only at temps. above 80°; a real spontaneous release of water took place above 95°. Peat contg. 84% water when heated to 100° without the application of pressure in 8 hrs. was dehydrated to 48.5% water. Intermittently aspirating dry air through the peat slightly increases the amt. of water carried off. On continuous aspiration of air through the peat mass there is a distinct drying effect at 40°. Heating for 8 hrs. and continuous aspiration gives a peat with only 22.8% water, which commercially is considered a completely dry product. Increasing the temp. to 100° does not give any further improvement. The changes taking place in the colloidal structure of the peat are demonstrated by the changes in the amts. of methylene blue absorbed. At 80° the supernatant fluid contains 5.5 times the amt. of the dye as in the case of non-treated peat; at 100° there is 16 times the amt. of dye left. At 80° the same amt. of dehydration and colloidal changes are obtained as with dehydration under pressure at 140-160°. A. MUTSCHELLER

A valuation of the peat beds of France. M. RICHMOND. *Oil Eng. Finance* **2**,

483(1922).—A discussion of the industry and a description of the principal deposits in France are given. D. F. B.

The lignite deposits of France. M. BRUNSCHWIG. *Oil Eng. Finance* 2, 483 (1922).—A description and analysis are given of the product from each of the 7 principal fields. D. F. B.

The storage of lignite briquets in supply bunkers. RUDOLF MÖLLER. *Feuerungstechnik* 10, 233-5(1922).—Fires in lignite briquet bins start in small areas, so that temp. measurements are not a preventive. Good ventilation of the bins is useful. The best plan is to divide the bins into easily emptied units holding one day's supply; a burning bin can then be used at once. Quenching with water is useless, with CO₂ impossible. Steam is the best quencher, but briquets so quenched must be used at once. Dusty briquets cause the most trouble. ERNEST W. THIELE

The coking of lignite. ROSENTHAL. *Feuerungstechnik* 10, 221-4, 235-9(1922).—A description of the lignite coking industry in central Germany. R. discusses: constituents of lignites suitable for coking; their occurrence; the construction of ovens and condensers; mode of operation; character and amt. of, and uses for, the products. ERNEST W. THIELE

The low-temperature distillation of lignites. M. LAFFARGUE AND R. JAUGEY. *Ann. mines* 12, 327-47(1922); cf. *Fuel* 124, 180. —A study of the most advantageous utilization of inferior fuels, such as lignite and coals contg. a high % of ash. The app. consisted of a vertical cast-Fe cylindrical retort elec. heated by a nichrome wire around the cylinder. Charging and discharging were at the top and bottom, resp. The distillate passed to a sep. condenser through a central tube. The temps. of the edge and center of the charge were measured pyrometrically. The charge was 15 kg. and the temp. in the center never over 800°. The results are tabulated, with descriptions of all the distillates obtained by fractional distn. of the tar. Contrary to accepted opinions it was found that the yield of oil from lignites increased at temps. above 550°. Only 2 lignites gave any amt. of oils below 400° and these were rich in paraffins and lubricating oils, with phenols in considerable amt. The max. yield of NH₃ was obtained when the temp. was 700-50°, and was greater for lignites than for coals. The production of NH₃ was reduced by heating rapidly to the required temp. Low-temp. carbonization was characterized by the max. temp. reached by the mass, and heating should be so regulated that the liberation of all products is complete at each temp. attained. Moreover these products should be removed from the hot zone immediately to prevent secondary decompn. In all expts. the optimum temp., that at which it is advisable to arrest heating to insure the best yields of oil and NH₃ without impairing the fluidity of the oils, was approx. 750°. This is a much higher temp. than is usually employed in low-temp. distns. Carbonization of lignite at low temps. did not give much more tar than at high temps., but there were much less pitch and more heavy and middle oils. The amt. of light oils was approx. equal to that obtained at higher temps., and the gas, though smaller in vol., was of a very rich quality. The expts. agree with previous investigators in that naphthalene and anthracene were absent in low-temp. tars, and in that phenols and paraffins were the predominating constituents. All the lignites left a semi-coke, in pieces of the same size and shape as those originally used for a charge (wood, etc.). This coke was considered suitable for gas-producer work. C. C. DAVIS

Benzene from lignite. HANS TRUTNOVSKY. *Braunkohle* 21, 445-8(1922).—The light hydrocarbon distillate from lignite was investigated by using activated α -charcoal (Bayer & Co.) as an adsorptive agent. The highest yield of benzene was obtained by distn. in a rotary drum app. From Köflacher coal, contg. 23.76% H₂O, was obtained 0.46% benzene (calcd. on dry wt.). This benzene was similar in phys. but

dissimilar in chem. properties to the analogous distillate from petroleum. It had d. 0.742, and had a very disagreeable odor. Two distns., dried separately, by KOH and KCl resp., gave the following data in %; fraction below 46°, 32.27, 38.06; 46-80°, 40.85, 45.55; 80-100°, 11.99, 1.83; residue above 100°, 7.94, 2.66; loss of non-condensable vapor, 6.95, 11.89. The dis., % C and % H for the fractions below 46° and at 46-80° resp. were: 0.7347, 0.7637; 85.04, 85.28; 14.96, 14.72. Two detns. of the mol. wt. of the 46° fraction gave 83 and 91, but these values are unreliable. The 80-100° fraction contd. 73.08% unsatd. compds. and the lower fractions chiefly unsatd. compds. It is inferred that this benzene is predominantly a mixt. of C_8H_{10} compds. which in the low fractions are mostly olefins and in the higher fractions partly cyclo-olefins.

C. C. DAVIS

Increasing ammonia output simultaneously with production of water gas in horizontal retorts. K. F. KRAU. *Gas u. Wasserfach* 65, 531-2; *Gas J.* 159, 645(1922).—Expts. were carried out to det. the possibility of making large amts. of water gas and at the same time increasing the NH_3 yield. By blowing steam at 0.05 atm. pressure into the coal, the NH_3 was increased 8-17%. By using steam at 3 atm. pressure, an increase of 25% was achieved together with a water-gas production equal to 30% of the coal gas made and an autocarburation of the water gas by means of the light constituents of the tar up to 110 B. t. u. per cu. ft. No increase in the CO_2 content was noted. Superheated steam (400°) increased the water-gas production, and also that of the NH_3 by 27%. The effect of the steam is to facilitate the release of the NH_3 from the coal, and the water gas dilutes the products of distn., increases their velocity in the retort, and thus lessens the danger of dissoc. of the NH_3 . Further expts., made by blowing water gas into the free retort space in order to cool it, increased the production of NH_3 by max. diln. and cooling of the distn. products, at the same time autocarburing the water gas injected up to 30 B. t. u. per cu. ft. The necessary cooling effect was obtained also by injecting steam into the free space up to 10% by wt. of the amt. of coal in the retort. The fallacy of recovering the N in the form of CN was also demonstrated clearly. This is due to the unprofitable recovery of the CN from the gas liquor, since it is impossible to avoid condensation of CN compds. when the gas is cooled and to recover the whole of the CN in the dry purification. The expts. demonstrate that water gas production is qual. equal in every way to that obtained in ordinary generators, and even really superior, considering the autocarburation.

J. L. WILEY

Ammonia from coal. J. W. COBB. *Fuel* 124, 167-74(1922).—Chiefly a review. Mention is made in a preliminary manner of new expts. on the mode of decompn. of known N compds. by heating, and the modifications brought about by the introduction of inorg. constituents present in coal ash. A study of $CH_3NH_2CO_2H$ showed that the evolution of NH_3 does not occur at a definite temp. but extends over a wide range. The solid residue as the temp. is raised alters in compn. and causes the N compds. present to become more resistant to the decompn. influences.

C. C. DAVIS

The generator gas space model. F. KRAEMER. *Fenerungstechnik* 10, 185-8 199-203, 211-4(1922).—K. assumes that the fuel is composed of C, H, and O, and that the ratio of the available H to the C actually burned is known. Gasification is to be conducted without adding anything but air and steam, and the gas formed is to be composed only of CO , CO_2 , H_2 , CH_4 , and N_2 (with H_2O vapor). The percentage of any 2 of these can be found if the other 3 are known. A space model can therefore be constructed, with percentages of CO , H_2 , CH_4 , or CO_2 , H_2 , CH_4 as coordinates. If on this model families of surfaces are constructed corresponding to const. air input (% of theoretical); const. steam input; const. theoretical flame temp.; and const. ratio of heat of combustion of gas to heat of combustion of fuel, all these surfaces are found to be planes. Directions and formulas for the construction are given.

ERNEST W. THIELE

Deposits in gas pipes and meters. R. L. BROWN. *Gas Age-Record* 50, 571-4 (1922).—The conclusion is made, from a study of the gummy deposits in meters distributing carburetted water gas, that the basis of formation of such compds. is the unsatd. hydrocarbons in the gas and that these hydrocarbons give rise chemically to the gum through polymerization, autoxidation, condensation or other chem. reactions. O in the gas undoubtedly plays a considerable role; in all gums O was found present up to 30-35%. The O oxidizes the hydrocarbons to indene and styrene; the gums are often acid and dissolved metals are often found with them. It is recommended that the content of O due to revivifying *in situ* be cut down and the boxes charged more frequently. More complete oil-cracking in the carburetter set is suggested as well as more complete removal of the tar before the purifiers and better condensing practice.

J. L. WILEY

Gasification of oil shales at the innsbruck gas plant. MAX SÖLLNER. *Gas u. Wasserfach* 65, 514-6; *Z. Ver. Gas Wasserfach* 62, 31-4, 35-8 (1922).—The shale was of poor quality being constituted of clay 30-40%, limestone 30-40%, org. material 3-20% and small amts. of S, N, P, alkalies, silicates, etc. By gasification, it yielded 15-20 cu. m. of 3000 cal. gas per 100 kg., 0.5 kg. tar, 80-85% residue, the remainder being H₂O and H₂O-sol. substances, and considerable S compds. It required 15% by wt. of coke for firing. The residue is suitable for making artificial building stone by further treatment in a lime kiln. A by-product, which has been made the subject of a patent, is CaS for use as a *dehairing agent in leather manuf.*

J. L. WILEY

Heat balance determinations on a benzene plant. F. PLENZ, K. BODE AND T. WERNER. *Gas u. Wasserfach* 65, 433-5, 447-9 (1922).—Results of tests made at the Karlsrue gas plant. Steam consumption per kg. of benzene was 5.48 kg., of which 65.4% was used in the preheater, 24.1% in the light oil sepn., 10.3% in the primary benzene distn.; and 0.2% in the secondary benzene distn.

J. L. WILEY

Cause and prevention of smoke in the boiler house. ANON. *Brick Pol. Trade J.* 30, 209 (1922).

H. G. SCHURECHT

Coal-tar oil and its uses. G. E. MARTIN. *Proc. Minn. Surveyors and Engrs. Soc.* 26 and 27, 93 (1921-22).—A general paper.

JACK J. HINMAN, JR.

Heat treatment of coke. S. R. GREENE. *Blast Furnace Steel Plant* 10, 456-7 (1922).—Over-quenched coke contains C of such a quality that it readily reduces CO, at comparatively low temps. near the top of the blast furnace. Such C, lost out the top of the furnace, results in not enough C getting down to the tuyères and the furnace goes cold at the hearth. Moisture content is not a criterion of proper quenching. Improvement in metallurgical coke can be expected as soon as some intelligent heat treatment is devised in place of the present crude accidental quenching methods. LOUIS JORDAN

Washing coal. E. COPPÉE ET C^{IE}. *Brit.* 183,463, July 18, 1922. App. for concentrating carbonaceous slimes, coal dust, and the like comprizes a mixer supplied with a weak current of H₂O, oil, and air for emulsifying the material, which is delivered by a pipe.

Concentrating coal. F. B. JONES AND MINERALS SEPARATION, LTD. *Brit.* 183,504, Feb. 22, 1921. Coal particles of linear dimensions between 0.1 and 0.5 in. are sepd. from shale or other gang, coating the particles with a film of oil and film flotation or sub-aeration flotation of the coated product. The oiling may be effected by agitating a pulp of coal and H₂O with an oil such as paraffin oil or fuel oil, or by immersing the coal in such an oil and then draining it. The coal may be first screened to sep. out the particles of the size referred to, or the whole of the crushed coal may be treated together. In some cases, a frothing agent such as cresol, may be added.

Motor fuel for aircraft. H. R. RICARDO. *Brit.* 183,449, April 7, 1921. A fuel

having a high latent heat in relation to its heat value is used at low altitudes, while at high altitudes this fuel is cut off and a normal hydrocarbon fuel is used. The special fuel may be that described in 183,577, or pure MeOH; or mixts. of EtOH and MeOH with H₂O; or EtOH 60, acetone 20, benzene 10, and H₂O 10%; or EtOH contg. over 3% of MeOH.

Motor spirit. H. R. RICARDO. Brit. 183,577, April 26, 1921. The preferred compn. consists of 60 lb. of EtOH, 20 lb. of acetone, 10 lb. of benzene, and 10 lb. of H₂O.

Motor spirit. J. D. RIEDEL, AKT.-GES. Brit. 184,785, July 6, 1922. A fuel for internal-combustion engines consists of a mixt. of a hydronaphthalene, an aliphatic hydrocarbon of low h. p., and methylated spirit, blended by a small proportion of ether or an alc.

Motor spirit. J. HAWES. Brit. 184,607. Alc. fuel is denatured by not more than 5% of PhNO₂. A suitable compn. consists of 96 vol. of 96-98% EtOH, 2 vol. of petroleum naphtha, 1 vol. of PhNO₂, and 1 vol. of AmOH. Petroleum naphtha may be omitted.

Pulverized fuel. C. E. BLYTH. Brit. 184,250, May 3, 1921. In a process for the combustion of pulverized fuel in which inflammable liquid such as paraffin is employed to enable low grades of fuel to be readily consumed when diffused in air, the liquid is added before or during pulverization of the fuel, in such proportions, which may be as low as 0.07%, that the fuel retains its property of diffusion in air in a finely divided state of suspension, the fuel and air acting as a vehicle for the liquid. In one arrangement liquid is allowed to drip into the hopper of a pulverizing machine such as is described in 175,301.

Briquet. C. JAEGER and M. W. ERICKSON. Can. 225,510, Oct. 31, 1922. A binder of condensed sulfite liquor and a small amt. of Ca(OH)₂ is thoroughly mixed with finely divided fuel; the mixt. is formed into briquets under high pressure and temp.

Coal briquets. W. W. STENNING, W. H. BEASLEY and MINERALS SEPARATION, LTO. Brit. 185,216, May 31, 1921. Finely divided coal is suspended in H₂O, mixed with a binding medium such as finely divided pitch with or without naphthalene, tar, etc., and is subjected to heat and to such agitation as will eliminate air to ensure the agglomeration of the coal particles. The coal under treatment is preferably suspended in the minimum of H₂O necessary to make a mobile pulp. The agglomerated material, which requires no special step other than draining to eliminate moisture, is briquetted while still hot. Cf. 122,454, and 155,875.

Peat. THERMAL INDUSTRIAL & CHEMICAL (T. I. C.) RESEARCH CO., LTD. AND J. S. MORGAN. Brit. 183,180, March 12, 1921. Peat, sewage sludge, or the like is heated in an autoclave to a temp. at which colloidal matter coagulates and is filtered without any substantial fall in temp. Steam is generated from the filtered peat and is used in the autoclave for heating the unfiltered peat and expelling liquid therefrom when it is on the filter. The partly dried product is removed from the filter by a scraper and enters a closed vessel contg. molten metal and having a valve loaded to ensure a temp. of about -160°. Then it is forced into a hunker and delivered to a briquetting machine. A lower moisture content than 15% may be obtained by using the waste peat from the flue gases of the furnace that heats the metal bath. Cf. 174,974.

Dry distillation. K. B. QUINAN. Brit. 184,451, July 21, 1922. Coal, shale, wood, etc. is distd. in a retort by the passage therethrough of hot gases which travel in a closed circuit comprizing a fan, superheater, retort and condenser. Condensates are collected in a tank and surplus gas escapes through a valve. The gas in circulation becomes satd. with vapors from distn. of the coal, etc., at the high temp. of the retort, and the lowering of the temp. of the gas in the condenser causes the deposition of all the

volatiles over and above the quantities in the gas depending upon the working temp. of the condenser.

Gas manufacture. J. A. YEADON. Brit. 185,684, Dec. 5, 1921. In the low-temp. carbonization of coal, finely ground coal, dried and partially heated, is fed continuously in a spray through a vertical retort having on its internal surface vertical corrugations extending for its full length. The working temp. is 400–700°; and the mechanical feeder is heated by waste heat from the retort flues or by a steam jacket. A revolving breaker at the end of the feeder sprays the fuel into the retort. A discharging water-cooled cylinder working continuously is arranged at the bottom of the retort. Cf. 114,971 (*C. A.* 12, 1831) and 127,986.

Gas manufacture; carbides. J. H. REID. Brit. 185,135, Feb. 22, 1921. In a process for the production of gas and CaC_2 from coal and other carbonaceous material and limestone the coal is heated to a temp. of about 2600–2800° F. so that the normally liquid volatile products produced are cracked and form gaseous products. The coal is first ground to a fineness of about 8 mesh and the limestone to about 40 mesh, and equal quantities of the ground materials are passed through a mixer to the distn. retort which is connected with an exhauster, condenser, and gas holder. The mixt. of coke and limestone produced is delivered, while still hot, through a crusher to an elec. furnace. A suitable construction is specified.

By-products from gas manufacture. A. ROBERTS. Brit. 184,507, Feb. 12, 1921. Into distn. gases is injected a substance to increase their vapor tension and control their temp. and the temp. of the gases is progressively lowered in stages by treatment at one stage with the cooler condensate of a later stage, whereby the by-products are fractionally removed. A suitable construction is specified.

Carbonization apparatus. E. STANFIELD. Can. 225,332, Oct. 31, 1922.

Distilling tar. THERMAL INDUSTRIAL & CHEMICAL (T. I. C.) RESEARCH CO. LTD., J. S. MORGAN, and D. RIDER. Brit. 184,624, June 7, 1921. In distg. tar by passing it below the surface of molten metal, the metal is either heated to such a temp. (about 350°) that the unvolatilized residuc is a hard pitch or is heated to 275–90° to obtain a pitch contg. anthracene. In the latter case, the pitch is afterwards sprayed with superheated steam to sep. anthracene, the vapors being cooled to 100–104° to sep. anthracene without condensing the steam. The volatile constituents may be fractionally condensed. Tar from a tank is pumped through a heat exchanger and fractionating column and enters the still beneath the surface of molten metal maintained at 275–90°. The vapors pass to the column which has a temp. of about 120°. Uncondensed vapors consisting of light oils and water vapors pass through the exchanger to a condenser. The condensate from the column passes to a second still containing molten metal kept at about 230°. The vapors pass to a heat exchanger and condenser and the residue to a cooler or to a third still maintained at about 270°.

Coking processes. WOODALL, DUCKHAM, & JONES, LTD. and SIR A. M. DUCKHAM. Brit. 185,461, May 3, 1921. In carbonizing fuel in vertical retorts with the introduction of steam into the bottom of the retort, the temp. of the coke at the lower end of the retort is maintained by introducing O or O mixed with a limited proportion of N together with or alternately with the steam. The Provisional Specification also states that a retort suitable for making O, *e. g.*, by the BaO process, may be heated by the waste heat from the vertical retort.

22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

The occurrence of petroleum in the Russian Carpathians. ANON. *Petroleum Z.* 8, 1029-35(1922).—An historical description covering the geology and development of this region. Oil from the Luga fields has d_{20} 0.840 and contains 10% paraffin. It congeals at 5°.

D. F. BROWN

The occurrence of petroleum in Holbenid Taman. B. BARTELS. *Petroleum Z.* 8, 989-92(1922).—An historical and geological description of the petroleum deposits in this section of Russia is given.

D. F. BROWN

Standardization of the testing of petroleum and its products. A. E. DUNSTAN. *Oil Eng. and Finance* 2, 439(1922); *Petroleum Times* 8, 565-6(1922).—A preliminary report of the committee on standardization appointed by the Inst. of Petr. Technologists. The findings and recommendations of the committee with regard to the various instruments and tests for petroleum and petroleum products are given.

D. F. BROWN

Notes on the use of super-centrifuges in the treatment of petroleum waste. E. DAVIN. *Mat. grasses* 14, 6259-63(1922).—A brief description of the Sharples super-centrifuge and of the theory of the app., showing its suitability for the sepn. of petroleum emulsions.

A. P.-C.

Note on the determination of the specific gravity of petroleum products. EMERYK KROCH. *Mat. grasses* 14, 6257-8(1922).—The d_{15} should be obtained from d_1 by means of the formula $d_{15} = d_1[1 + a(t-15)]$; but Engler-Höfger, Kissling-Erdöl, and others give $d_{15} = d_1 + a(t-15)$, which involves an error of 1-3 units in the third decimal place.

A. P.-C.

Notes on the determination of absolute viscosity of petroleum oils. W. H. FULWEILER AND C. W. JORDAN. *J. Ind. Eng. Chem.* 14, 723-4(1922).—A medicinal oil at 37.78° had a viscosity of 40.36 cp. but on standing 24 hrs. in the viscosimeter the viscosity decreased 0.54% and after 3 months it decreased 0.42%. Another petroleum oil increased in viscosity by 0.42% in 24 hrs. Castor oil showed an increase of 0.33%, while hard oil showed a decrease of 0.3% after 24 hrs. Exposure of filtered oil to light caused no change but unfiltered oil increased in viscosity by 1% in a week. An adsorbed film on the glass is suggested as a possible explanation.

EUGENE C. BINGHAM

Iodine value of petroleum oils. SEIJI KAWAI. *J. Chem. Ind. (Japan)* 25, 406-19(1922).—I values of Akita oil 1 ($d_{15.5}^{15.5}$ 0.9242), oil 2 (b. 300-400° $d_{15.5}^{15.5}$ 0.9397) and Nishiwara oil (b. 350°, $d_{15.5}^{15.5}$ 0.9162) were detd. under various conditions by the Wijs, Hübl and Hanus methods. The more solvent (CCl_4) used, the greater I values are obtained, other conditions being const. When the amt. of oil is variable, I value changes reciprocally with the oil; when the amt. of I soln. is variable, I value changes directly proportionally with the amt. With 25 cc. I soln., 0.3 g. sample, 10 cc. CCl_4 and 30 min. absorption, the I values obtained were at 5° 38.57; 10° 39.92; 15° 41.93; 20° 44.11; 25° 46.54; 30° 49.26. During 1 hr. absorption increases rapidly; after 2 hrs., the absorption is comparatively slow, values increasing indefinitely with the time of absorption, the general nature of the curve of this increase being same for all the oils used. With petroleum oils the Hübl value is less than $1/2$ of the Wijs, while the Hanus value is slightly greater than the latter. The effects of these conditions are same regardless of what I soln. is used. In giving the I value of petroleum oils, therefore, it is necessary to specify these conditions.

S. T.

Greater part of Argentine crude equals light Mexican oil. ANON. *Nat. Petroleum News* 14, 45, 87(1922).—Light Mexican oil will top as high as 10-17% low-grade motor fuel as compared with about 5% for the Argentine product. Oil from the Neuquen district, Argentine, however, tests 36° Bé. and compares favorably with some of the

U. S. Mid-Continent high gasoline oils. Oil from the Comodoro Rivadavia district is 21.0° Bé. at 60°, flash point (Pensky-Martens) 90° F., S 0.187%. It is black and has a sweet odor. When it is topped of its gasoline and kerosene it yields water 4.9%, 57.1° Bé. gasoline 5.0, 41.0° Bé. kerosene 6.8, 33.2° Bé. gas oil 1.8, 18.0° Bé. fuel oil 80.8; loss 0.7. Neuquen crude yields 50° gasoline 25.0%, 45° kerosene 9.0, 39° gas oil 5.0, 24° fuel oil 59.0; loss 2.0.

D. F. BROWN

Crude oil. J. B. RATHBUN. *Petroleum Age*, 10, No. 9, 39(1922).—A compilation of analytical data covering Texas crude oil from the various fields of that region.

D. F. BROWN

Success of calorizing in oil refining. B. L. JARRETT. *Oil Gas J.* 21, No. 24, 82-4 (1922).—Steel tubes are calorized by coating with aluminium. Runs 20% longer in the oil cracking are possible with calorized equipment. The corrosive action of S and its compds. as well as of C itself on the steel is prevented.

D. F. BROWN

Developments in the manufacture of natural-gas gasoline. F. E. HOSMER AND F. M. SEIBERT. *J. Ind. Eng. Chem.* 14, 1106-11(1922).—A low-pressure evapn. process is described, which effects considerable saving in power costs. Gas from the field is compressed to 70-125 lbs./sq. in. After passing through an accumulator, the gas passes downward through the inner pipe of a double-pipe coil, into a 2nd accumulator. From this the gas is delivered to the fuel lines. Gasoline from accumulators is introduced into the bottom of the outer pipe of the double-pipe coil, and is evapd. by being connected with the intake side of the vacuum pump which gathers the gas from the field. The gasoline vapor is thereby mixed thoroughly with the incoming gas. The use of crude oil as absorbent medium in a standard process is described. This process furnishes an improved method for transporting casinghead gasoline to the refinery, since the crude with its dissolved casinghead constituents is pumped through the pipe-lines.

W. F. FARAGHER

Refining gasoline and kerosene by hypochlorites. A. E. DUNSTAN AND B. T. BROOKS. *J. Ind. Eng. Chem.* 14, 1112-5(1922).—The process described is applicable for desulfurizing all the gasoline and kerosene distillates from all types of crude petroleum. Losses and refining costs are lower than those of the methods in general use. A concn. of 12-15 g. of available Cl per l. is employed. Electrolysis of NaCl soln. has been abandoned, and the use of liquid Cl and alkalis substituted. Mixing is effected by pumping the soln. of hypochlorites from the bottom of the agitator, and discharging it below the surface of the distillate. Lead lining is not used in the agitators. Some of the oxidation products are sol. in H₂O, and others are removed by calcined bauxite or fuller's earth, etc.

W. F. FARAGHER

The manufacture of lubricating oils. F. N. WILLIAMS. *Refiner & Nat. Gasoline Mfr.* 1, No. 2, 12-20(1922).—A brief outline of methods used in the manuf. of lubricating oils and stocks is given. Numerous data charts give comparative tests of various cylinder oils, comparative tests on Ranger crude before and after treating, yield of cylinder stock from Ranger crude and tests on same, av. tests on Muskogee crude, a complete running chart on the latter, distn. of Electra and West Columbian crudes, and runs.

D. F. BROWN

The New Albany shales of Indiana. J. R. REEVES. *Bur. Mines, Repts. Investigations* No. 2390, 8 pp.(1922).—The principal oil shale of Ind. is known as New Albany shale. Normal thickness of shale beds is about 100 feet. Microscopic examn. of thin sections of shale reveals resinous appearing spores and spore cases. Typical New Albany shale contained moisture 0.82, volatile matter 15.86, fixed C 5.54, ash 77.78, total S 4.36%. The shale yields 6 to 14 gals. per ton of oil of d. 0.940. Viscosity at 130° F. 43. Percent tops 47.6 (distg. up to 275°). Av. N content 0.5%, equal to 42.5 lbs. of (NH₄)₂SO₄ per ton. K content is too low to be of commercial value.

R. T. GOODWIN

A new apparatus for distillation analysis and experiments with oil shale. WÖBLING. *Braunkohle* 21, 453-4(1922).—An inclined porcelain tubular retort in an elec. oven was found to be the most effective app. for distg. oil shale on an expld. scale. By distg. 400 g. of shale for 3-4 hrs. with 2 kw.-hrs. power consumption, a yield of tar was obtained greatly exceeding that from any other type of app. A hydrocarbon residue of only 1.5% was left. The H_2O and tar distd. over were condensed in a modified Pelicot condenser, and the gases were freed from H_2S and CO_2 by $Pb(OAc)_2$ and KOH , resp., simplifying the subsequent analysis. Oil shales from various localities showed great differences in tar, the consistency varying from a thin liquid to solid. The light oil contents were in general low, whereas the oils from 150° to 250° reached 30-40%, with thick oils from distn. *in vacuo* up to 300° approx. the same, and a pitch residue of 10-20%. Towards 300° decompn. became considerable, and the distillate became deep red. The content of alkali-sol. constituents was in general only about 5%. Treatment with H_2SO_4 caused considerable resinification. By preliminary removal of the basic compds. with dil. H_3PO_4 , this did not occur. The S content varied greatly. Even with long heating with Zn dust, the % S could not be reduced, and distn. of the shale with Fe failed to decompose the org. S compds. High mercurization and I nos. indicated considerable % of unsatd. compds., differentiating the shale tar fundamentally from petroleum.

C. C. DAVIS

Gasification of oil shales at the Innsbruck Gas Plant (SÖLLNER) 21. Purifying oils (Brit. pat. 185,247) 27. Dry distillation (Brit. pat. 184,451) 21.

Purifying mineral oils. C. R. EHLERS. Brit. 184,991, July 29, 1921. Petroleum oils are freed from resinous, tarry, and bituminous substances by agitating for say an hr. with 30-70% of toluidine, xylidine, aniline or other aromatic amine with a benzene nucleus, allowing to settle, and sepg. the upper layer of refined oil. The amines may be produced by nitrating the aromatic hydrocarbons obtained from anthracite coal-tar and reducing the nitration products; or a raw material, such as anthracite coal-tar distillates, contg. these amines may be used. The refined oil may be freed from any traces of amine by treatment with steam.

Purifying mineral oils. A. C. NESFIELD. Brit. 183,527, March 24, 1921. An app. for desulfurizing oils by treatment with Cl comprises a series of superposed reaction chambers down the sides of which the oil films on to annular baffles and over conical deflectors spaced apart from disks and hollowed out to form chambers and peripheral slots through which the Cl from inlet pipes and passages passes to burst through the films; to wash the films on the sides of the chambers and to pass to the next chambers. In each chamber the treated oil is mixed by annular baffles. From the lowermost chamber the oil is passed to a tank contg. H_2O , in which the pptd. S settles and above which the purified oil collects. Jackets may be used to heat the chambers and the oil and Cl may be preheated. The upper end of the topmost chamber may be extended and arranged to form a reservoir for preheated oil and a condenser for vapors from the reaction chambers. Powdered lime may be fed into this reservoir by a worm or other device, and the mixed oil and lime after treatment be passed through a cooler and filtered to sep. pptd. S and bituminous matter. The treatment may take place simultaneously with the fractionating or distn. of the oil.

Refining oils. A. E. DUNSTAN. Brit. 184,281, May 12, 1921. The desulfurization of liquid hydrocarbons by treatment with alkali hypochlorite and free alkali is preceded, followed or both preceded and followed by treatment with alkali. The treatment may be effected in a vessel in which brine is being electrolyzed for the production of $NaOCl$, and the temp. may be raised to $120^\circ F$. The product may be filtered through animal charcoal, fuller's earth, or dehydrated Al_2O_3 .

The treatment of hydrocarbons. A. T. STUART. Can. 225,671, Nov. 7, 1922. Hydrocarbon oils are treated at 600° and several atms. pressure with about 4% of their wt. of H and the reaction products are recovered.

Cracking hydrocarbons. UNIVERSAL OIL PRODUCTS CO. Brit. 185,439, March 11, 1921. In converting heavy into light hydrocarbons as described in 160,236, the primary heating zone is maintained at temps. up to 875° F. and the pressure is maintained at about 135 lb. per sq. in. so that at least 45% of the oil is converted into a distillate with a min. gravity of 45° Bé. A suitable app. is specified.

Cracking hydrocarbons. C. A. JENSEN. Brit. 185,624, Aug. 27, 1921. An app. for cracking oils comprises 2 concentric chambers which are used alternately as cracking chambers and as heating chambers, the C deposited during cracking being burned when the chamber is subsequently used for heating. The chambers are packed with catalytic, absorbent, or spreading materials, such as cast iron, Ni, or other metal, porous fire-clay, fire-brick, fuller's earth, etc.

Cracking hydrocarbons. F. G. NUGGE. Brit. 185,632, Sept. 7, 1921. The oil is pumped through a preheating pipe into the base of a column of molten material such as Pb, contained in a vessel in a furnace chamber. Vapors pass from the upper part of the vessel to a condenser and the uncondensed gases are withdrawn from the receiving vessel by a pump and are injected into the molten material through pipes. Additional hydrocarbon gases may be supplied through a pipe. The preheated oil is injected into the molten metal under a hood and the stream of liquid and vapors is broken up by perforated baffles, which also serve as stays for the pipes. The molten metal may be heated to 400-750°, and the app. maintained under a pressure of 150 lb. per sq. in.

Apparatus for the decomposition of hydrocarbons. A. T. STUART, and G. N. MIDDLETON. Can. 225,672, Nov. 7, 1922.

Rotating electrode dehydrator for petroleum emulsions. H. C. FIDDY. Can. 225,385, Oct. 31, 1922.

Removing oil from oil sand. E. K. DAVIS. Can. 224,766, Oct. 17, 1922. The sand is heated during agitation, a heated solvent is forced through the sand to remove the oil and the sand is heated to drive off the solvent.

Distilling shale. L. KERN. Brit. 183,823, July 21, 1922. In the distn. of shale and similar materials the shale is ground and briquetted and the briquets are placed in a retort so that air passages are left between them, after which they are uniformly and slowly heated to at least 700°; the air passages facilitate the escape of the oil vapors, and the slow heating prevents fusion of the flux-forming constituents. After the bitumen has been driven off, air is passed into the retort and heating continued to about 1050°. A porous product is formed suitable for insulating purposes or as a substitute for kieselguhr. The ground shale may be mixed prior to distn. with peat, sawdust, or the like, and with substances which yield acids, such as chlorides, more particularly $MgCl_2$, the acids acting on the bitumen.

23—CELLULOSE AND PAPER

CLARENCE J. WEST

Reactions of cellulose with sodium chloride and other neutral salt solutions. I. Preliminary survey. HELEN MASTERS. *J. Chem. Soc.* 121, 2026-34(1922).—When cotton, thoroughly washed with H_2O to remove sol. material, is treated with a neutral soln. of NaCl, the ext. is always acid to methyl orange. Upon repeating the extn. the amt. of acid rapidly decreases and after 2-3 extns. the ext. became neutral. If, however, the treated cotton is washed with H_2O and again treated with NaCl soln., an acid

ext. is again obtained. In 1 expt., 10 g. cotton, washed with 100 cc. 0.1 *N* NaCl, gave 3.9 mg. HCl. 0.01 *N* NaCl extd. about 3 mg. HCl. A boiling NaCl soln. did not remove more acid than one at room temp. NH_4Cl and Na_2SO_4 gave results similar to those with NaCl. The amt. of acid extd. with BaCl_2 and also with CaCl_2 was considerably less than that extd. by NaCl, the av. amt. in each case being 2.3 mg. HCl. With CdI_2 the amt. of acid extd. averaged 1.2 mg. HCl. The H_2O used to wash the cellulose after salt treatment is alk., contg. alkali equiv. to the acid found in the NaCl soln. With CdI_2 the washings did not become alk. Acid was also liberated when a soln. of HCO_2Na (slightly alk. to litmus) was passed through washed cotton. The reaction thus appears to be typical of the behavior of a no. of neutral salts. C. J. WEST

Cellulose. VII. Cellulose-copper compound. KURT HESS, ERNST MESSMER AND E. JAGLA. *Ber.* 55B, 2432-43(1922); cf. *C. A.* 16, 2027.—The optical activity of solns. of cellulose in ammoniacal $\text{Cu}(\text{OH})_2$ decreases with decreasing concn. of the $\text{Cu}(\text{OH})_2$ or the cellulose, the NH_4OH content being const. The values obey the mass action law, on the assumption that 1 mol. $\text{Cu}(\text{OH})_2$ is associated with a mol. $\text{C}_6\text{H}_{10}\text{O}_5$. Similar results are obtained with the biase-anhydride obtained from cellulose, $\text{C}_6\text{H}_5(\text{OH})_2$ and mannitol. The ppt. obtained by addition of excess of NaOH to the above solns. gives figures for the ratio: 1Cu : 2Na : 12C, that is, $\text{Na}_2(\text{C}_{12}\text{H}_{16}\text{O}_{10}\text{Cu})$. This ratio is the same as obtained by Normann (*Chem.-Ztg.* 30, 584) for the product of the digestion of cellulose with $\text{NaOH}-\text{Cu}(\text{OH})_2$, which work has been confirmed. It also agrees with the results of Traube (*Ber.* 55, 1899). C. J. WEST

Symptoms among workers handling celluloid and its solvents. F. HEIM, E. AGASSE-LAPONTE, AND A. FEIL. *Paris Medical* No. 23, 477 (June 3, 1922); *Bull. office intern. d'hyg. publ.* 14, 995 (Aug. 1922).—Only one clinical symptom, headache, and one hematological indication, eosinophilia are the result. JACK J. HINMAN, JR.

Modern practice in manufacture and applications of steamed ground wood. A. O. BRAGG. *Chem. Met. Eng.* 27, 793-7, 842-6(1922).—Steaming wood before grinding causes partial soln. of H_2O -sol. materials, org. acids, alcs., gums, sugars, etc., and the softening into a gelatinous, adhesive condition of the remaining gums and mucilages. Hydrolysis of the lignin components of the wood also occurs in part. These cause a loosening of the fibers so that the stones do not disintegrate them so much. Density plays a part in the time of steaming. Woods of about 27 or 28 lb. per cu. ft. density should be steamed at 35 lb. pressure for 20 hrs. and higher density woods in proportion. Equipment and its operation are discussed. The no. of variables influencing cooking conditions are very large; among these are moisture content of wood, pitch or rosin content, seasoning of wood, density, soundness and freedom from decay, diam. of logs, color of pulp desired, etc. Scrub and white pines are now used for wrapping paper, being cooked 9-16 hrs. at 13-20 lb. gage. Yield of ground pulp is about 2200 lb. per cord of wood. For the wrapping paper mentioned above 60% sulfite and 40% steamed ground wood are furnished. Boards may be made from steamed spruce (50-55 lb. for 14 hrs.) or a mixt. of birch and maple. Steamed hardwood is of small tensile strength, tender and likely to cause trouble in lapping and on machine. When dry it makes a very rigid but brittle sheet. It may be used with cooked spruce or with sulfite in boards. Steaming hardwoods and pitchy woods, neither of which give satisfactory ground wood in the untreated state, would seem to offer fields for wider use of the steaming process, to replace, in part, unbleached sulfite in locations where few of the local woods are adapted to the sulfite process. C. J. WEST

The use of chlorine in the manufacture of paper pulp. C. ARDISON DE PERDIGUIER. *Papeterie* 44, 866-73(1922).—Polemical against Pomilio (*C. A.* 16, 3544).

A. P. C.

Determining the tensile strength of paper. RAYMOND FOURNIER. *Papier* 25,

437-40(1922).—F., after briefly discussing the shortcomings of the instrument generally used for measuring the tensile strength of paper (Schopper), advises using a machine which could take a much wider test strip, e. g., 15 cm. instead of 15 mm. This would necessitate the use of forces up to about 300 kg., and Schopper type instruments of this capacity would be too heavy, cumbersome, and expensive. A simple and efficient hydraulic type of instrument is described in which the tension is exerted by means of a piston displaced by screwing a rod into the cylinder carrying the piston. A. P.-C.

Nature, treatment and qualities of straw pulp. E. ARNOULD. *Papier* 25, 433-5 (1922).—General review. A. P.-C.

Cellulose derivatives. PLAUSON'S (Parent Co.), LTD. Brit. 183,908, April 28, 1921. Cellulose derivs., such as acetates, ethers, and H_3PO_4 and S compds., are prepd. by subjecting cellulose to high-speed mechanical disintegration, and treating the colloidal and highly dispersed cellulose so obtained with suitable chemical reagents. In example, cotton is dispersed in H_2O in the colloid mill until the particles have a diam. of 0.8μ , and then combined with H_3PO_4 at $30-50^\circ$, and preferably after the addition of a trace of H_2SO_4 . Alternatively, the H_3PO_4 may be allowed to react during the dispersion of the cellulose; dispersed cellulose is heated with Ac_2O and $AcOH$ in the presence of $AcONa$ as the accelerator, and the $AcOH$ may be produced in the nascent state by means of $AcONa$ and H_2SO_4 ; dispersed cellulose is heated with S, preferably in the presence of caustic or carbonated alkali and at a temp. not exceeding 150° ; dispersed cellulose is mixed with $MeOH$, and HCl gas introduced—a methyl ether of cellulose is formed.

Cellulose esters; artificial threads; films. J. DUCLAUX. Brit. 184,197, Feb. 1, 1921. To a soln. of a cellulose ester there is added in a relatively volatile org. solvent a small quantity of a nonvolatile org. solvent sol. in H_2O , and after formation of thread, film, etc., by the evapn. of the volatile solvent, the nonvolatile solvent is extd. by washing with H_2O . Formamide, acetamide, chloral, and chloral hydrate may be employed as nonvolatile solvent; the vol. solvent may be methyl, ethyl, butyl, or amyl formate or acetate, together with $MeOH$ or $EtOH$.

Cellulose-acetate products. H. DREYFUS. Brit. 184,671, July 20, 1921. Cyclobutanone or side chain homolog thereof, such as dimethyl- or diethylocyclobutanone, is employed as a solvent for cellulose acetates in the manuf. of solns., plastic masses, artificial silk, films, etc. The solvents, diluents, filling substances, coloring matter, etc., may be added in addn. Examples of proportions are given in the Specification.

Celluloid. P. BALKS and G. LEVSHOFF. Brit. 181,697, May 24, 1922. Waste pieces of cellulose derivs., such as nitrocellulose, acetylcellulose, ethylcellulose, etc., or of these substances made plastic with gelatinizing media, are worked directly into finished articles by rendering the mass plastic by pressure and heat, molding small bodies of approx. the required dimensions, and finishing the article in dies under pressure and heat. The waste may be powdered or made plastic directly by heat and pressure. Ornamented articles may be produced by pressing a layer of paper, fabric, plastic masses, etc., carrying the desired design, between two or more transparent layers of the plastic mass before the preliminary pressing. Cf. C. A. 16, 3758.

Viscose; artificial silk; films. H. DREYFUS. Brit. 183,882, Feb. 9, 1921. Cellulose, or a conversion product of cellulose, together with caustic alkali in a concn. of 15% and upwards, preferably 20-50%, and in a quantity of not more than 2 mols. of caustic alkali, preferably 1 mol. or less, per mol. of cellulose, is treated with CO_2 in a quantity of not more than $1/2$ mol. per mol. of cellulose. The CO_2 is used in the presence of benzene or other solvent, or diluent for CO_2 . The viscose produced is sol. in H_2O or in alkali, and may be spun without ripening. When it is used for the spinning of artificial silk or in the manuf. of films the following coagulating baths may be employed: bi-

sulfates or mineral acids, or weaker acids such as HOAc or formic acid, or stronger acids such as oxalic acid alone or together with such weaker acids, or alkali bicarbonates; with these weaker acids or alkali bicarbonate baths, the temp. of these is preferably raised to 30-40°.

Viscose; artificial silk; adhesives; plastic compositions. PLATON'S (Parent Co.), LTD. Brit. 184,533, April 11, 1921. Viscose is prepd. from cellulose rendered colloidal by high speed mechanical disintegration, as by grinding in the colloid mill in the presence of a liquid dispersion medium, preferably a soln. of NaOH; to the alkali-cellulose so obtained, CS₂ is added, and the reaction continued in the same app. with vigorous beating. By this process, smaller quantities of alkali and CS₂ are necessary, and quantities of the former may be employed corresponding to the monosodium and disodium viscoses; further, ripening of the viscose is either unnecessary, or may, in the case of artificial silk, be reduced to a few hrs. Plastic masses may be obtained by heating to 80-100° the viscose soln. prepd. as above described or with which has been incorporated, during the dispersion stage, substances such as resin or rubber, which modify the properties of the product. By the addition of NaCl or other inert electrolyte, a product in the form of a fine powder, after washing and drying, is obtained suitable for molding. An *adhesive* may be prepd. by adding starch during the dispersion stage. The soln. may also be evapd. to give a dry water-soluble product, stable *in vacuo* or in an inert gas such as N or H; in air, the dried product changes slowly and becomes irreversible.

Paper pulp. G. A. MOURLAQUE and J. J. B. PARENT. Brit. 185,421, Aug. 31, 1922. Vegetable material is transformed into pulp suitable for paper, etc., by treatment with O. The divided and moistened wood, etc., is preferably placed in an autoclave and O, which may be ozonized and obtained from liquid air, is led in under a pressure of 2-5 atms. for 3-6 hrs. Alternatively, the O may be generated in the autoclave by dissolving Na₂O₂ in H₂O or by the action of H₂SO₄ on Na₂O₂ or BaO₂.

Solidifying fibrous pulp. B. NISHINA. Brit. 185,399, Aug. 4, 1922. Fibrous pulp mixed with adhesive material is solidified in thin film by projecting it under high pressure from spouts on to a slowly moving surface of gauze, felt, etc. After drying, the material is removed from the surface and calendered on rolls or pressed into molds. Alternatively, the pulp may be left adhering to the surface, which then serves as a reinforcement. The process is suitable for making materials such as pasteboard, papier maché, artificial leather, belting, linoleum, and flooring.

Vulcanized fiber. J. A. SUTCLIFFE. Brit. 183,497, Jan. 27, 1921. Vulcanized fiber prepd. by the ZnCl₂ process is treated after vulcanization with a strong soln. of NH₃ to render it non-hygroscopic.

Chemistry of the polysaccharides (PRINGSHEIM) 28. Waterproofing (Brit. pat. 184,462) 18.

24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE.

The ignition of gases. II. Ignition by a heated surface. Mixtures of methane and air. WALTER MASON and R. V. WHEELER. *J. Chem. Soc.* 121, 2079-91 (1922).—The ignition temp. of a gaseous mixt., as ordinarily detd., is not an abs. quantity since it is effected by the nature and extent of the solid igniting surface. To det. the compn. of the most readily ignited mixt. of CH₄ and air at atm. pressure, a quartz tube of 81 cc. capacity was used as a container for the various mixts. Under these conditions air contg. 5.85% CH₄ ignited at 695° while other samples both richer and poorer in CH₄ required higher temp. For gas of a given compn. the temp. of ignition is lowered by increasing

the size of the contg. vessel. The "pre-flame period" or "lag on ignition" is the time interval between the introduction of the gas to the hot tube and the appearance of flame. This lag is quite appreciable for CH_4 -air having a value of about 10 sec. at 650° . The duration of this period decreases with decreasing CH_4 concn. and with increasing temp. Cf. C. A. 14, 3157.

J. A. ALMQUIST

Explosives. E. I. DU PONT DE NEMOURS & Co. Brit. 184,487, Aug. 11, 1922. A blasting explosive contg. from 3 to 15% of H_2O is made by grinding smokeless powder (mainly nitrocellulose) and cordite (mainly nitrocellulose and nitroglycerin) with H_2O and then mixing them together preferably with the addn. of a nitrate, such as Na nitrate, and chalk. The smokeless powder used contains nitrocellulose with 2% of residual solvent and 0.5% of a stabilizer such as diphenylamine.

Explosive. G. WÄGER. Can. 225,479, Oct. 31, 1922. A blasting cartridge contains a mixt. of combustible org. material capable of absorbing liquid air with a combustible metallic powder, inserted in an envelope and impregnated with liquid air.

Signal rockets. W. BOEHM. Brit. 184,715, Sept. 19, 1921. Signal rockets are loaded with Mg or like metal in the form of thin foil, ribbons, wigs, or woven fabrics of these, to which may be added flame-coloring salts preferably impregnated into a Mg texture. This charge is ignited by a priming compn. consisting of black powder mixed with Mg powder.

25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

The life and works of Paul Dosne. ALBERT SCHEURER. *Bull. soc. ind. Mulhouse* 88, 417-20 (1922).—An obituary, with a list of articles published from 1877 to 1920.

A. P.-C.

The acid alizarin dyestuffs. J. I. M. JONES. *J. Soc. Dyers Colourists* 38, 201-3 (1922).—A brief history of the discovery and development of these dyes.

CHAS. E. MULLIN

Steam waste in dyeing and finishing. ANON. *Textile World* 62, 2161-3, 2191-2 (1922).—A discussion of losses due to defective equipment and poor practice.

CHAS. E. MULLIN

A discussion of dye testing. R. E. ROSE. *Color Trade J.* 11, 199-201 (1922).—The discussion points out the unreliability of the testing methods now in use and the necessity for more coöperative research work.

CHAS. E. MULLIN

Dyeing of fast shades on wool by the chromosol method. GIOVANNI TAGLIANI. *Color Trade J.* 11, 158-9; *Textile Colorist* 44, 650-2 (1922).—A discussion of the use and advantages of the mordant chromosol, which is a double oxalate of Cr and Na.

CHAS. E. MULLIN

Dyeing wool in fast colors. B. WUTH. *J. Soc. Dyers Colourists* 38, 241-8 (1922).—A historical sketch of the developments in dyeing fast colors on wool, together with discussions of the relative advantages and disadvantages of the various processes used.

CHAS. E. MULLIN

Dyeing of cellulose acetate silk. W. E. SANDERSON. *J. Soc. Dyers Colourists* 38, 162-5; *Am. Dyestuff Rep.* 11, 6-9 (1922).—The subject is discussed generally and some details are given regarding the use of about 60 dyes.

CHAS. E. MULLIN

Direct cotton black X with green undertone. H. HERLINGER. *Color Trade J.* 11, 144-5 (1922).—Pure H-acid must be used to produce the green tone; instructions are given for making the pure product. The effects of other impurities were studied and details are given for the manuf. of direct black X.

CHAS. E. MULLIN

Some notes on the early indigo industry in the South. B. B. ROSS. *J. Ind. Eng. Chem.* 14, 1153-4 (1922). E. J. C.

The scientific kier boil. FELLOWS. *Color Trade J.* 11, 165-7 (1922).—The use and advantages of *sol-esco* are described. CHAS. E. MULLIN

Some important but overlooked properties of cotton, mercerized by means of sodium hydroxide or sodium chromite (alkaline chrome mordant). JOS. POKORNY. *J. Soc. Dyers Colourists* 38, 248-50 (1922).—Mercerized cotton has slightly basic properties similar to the basic properties of wool and hence an affinity for acid and direct colors from hot or cold dil. acid solns. Expts. suggest that possibly all sulfonated azo or carboxylated dyes may be applied to mercerized cotton from a 1% AcOH bath at 80-90°. The fastness compares favorably with dyeings made in the usual manner. The acid treatment after mercerization very materially decreases the affinity of the dyes mentioned for the cotton, possibly showing the formation during mercerization of an active but labile basic compd. which is destroyed by the acid. Cotton treated with Koechlin's alk. chrome mordant also possesses basic properties, but in this case they are more pronounced owing to the presence of Cr compds. This cotton will fix deeper shades than the unmercerized cotton, of all acid dyes, including direct, from hot or cold dil., neutral or slightly acid baths. It exhausts all azo dyes, except the basic, and the more sulfonated the dye, the easier the dyeing. Sulfonated or carboxylated triphenylmethane or anthraquinone derivs. are also fixed and many colors are fast to washing. Fastness may be increased by steaming or compd. mordanting with Cr + Cr, Cr + Al and Cr + Ni. Diazo and tetrazo compds. may be fixed on the mordanted cotton by simple immersion in cold aq. soln. followed by coupling with a naphtholic compd. Org. intermediates such as H and J acids may also be fixed by suitable treatment. The alk. chrome mordant is prepd. by dissolving 1 kg. Cr alum in 5l. H₂O, cooling to 10° and pouring into 2.5l. NaOH (d. 1.360) cooled to 10°. CHAS. E. MULLIN

Method of determining grease and dirt in wool. D. A. SPENCER, J. I. HARDY AND M. J. BRANDON. U. S. Dept. Agr., *Bull.* 1100, 1-20 (1922).—Before the scouring process all samples of wool are brought to a const. moisture content by drying at 50° for 3 hrs. Grease is removed by 3 successive treatments with gasoline which is drained off through filter paper in order to retain all foreign matter. Dirt is removed by means of soap and water at a temp. of 40-5°. W. H. ROSS

Acid treatment of wool scouring wastes. H. M. LADELL. *Public Works* 53, 90 (1922).—Acid is added in tanks with 3 times the day flow. One gal. acid is used per 250 gal. suds. LANGDON PEARSE

Dyes. F. W. ATACK AND C. W. SOUTAR. *Brit.* 185,137, Feb. 23, 1921. Halogenated *N*-dihydro-1,2,2',1'-anthraquinoneazines, which have been prepd. by condensation of halogenated aminoanthraquinones in presence of a Cu salt, are purified by treatment with halogen or substances yielding halogen; the treatment may take place in the liquid in which the formation of the dyestuff has been effected. In an example, 3,3-dibromo-*N*-dihydro-1,2,2',1'-anthraquinoneazine is chlorinated at ordinary temps. in nitrobenzene suspension, warmed, and the dyestuff filtered from the impurities which pass into soln.

Dyes. NATIONAL ANILINE & CHEMICAL CO., INC. *Brit.* 183,419, Dec. 14, 1921. Pure dibenzanthrone is obtained by treating the crude product of alkali fusion of benzanthrone with Na₂S₂O₈, sep. the dissolved leuco compd. from the insol. residue, and reoxidizing by air. It may be further purified by extr. with C₆H₄Cl₂. The alkali fusion may be effected in the presence of an inert diluent, e. g., kerosene, and a reducing agent, e. g., dextrin. The purified dibenzanthrone gives a green dye on nitration, while the insol. by-product gives a gray nitration product.

Dyes. BADISCHE ANILIN & SONA-FABRIK. Brit. 184,193, Aug. 4, 1922. A blue vat dye, distinguished by its fastness to Cl and hypochlorites from the known commercial product made by alkali fusion of β -aminoanthraquinone, is obtained by the following alternative modifications: (1) β -Aminoanthraquinone which has been freed from such impurities as yield products not fast to Cl is subjected to alkali fusion. This may be obtained by dissolving the commercial article in concd. H_2SO_4 and dilg. with H_2O or weaker acid so as to ppt. β -aminoanthraquinone sulfate but not the impurities; the sulfate is then decomposed by H_2O ; the crude amine may also be treated with weaker acid which will dissolve the undesired impurities. (2) The alkali fusion is effected under such conditions as will destroy the portions not fast to Cl, *e. g.*, by increasing the temp. or time of fusion, or by addition of oxidizing agents. (3) The known commercial dye may be treated to remove those constituents not fast to Cl, *e. g.*, by soln. in H_2SO_4 and diln. so as to ppt. the dye but not the impurities. Two of these processes may be employed conjointly and the products may be subjected to the known treatment with alk. reducing agents. Examples of the various methods are given.

Dyes. BRITISH DYE STUFFS CORPORATION, LTD., A. G. GREEN, A. G. SAUNDERS, K. H. and S. C. BATE. Brit. 185,612, Aug. 17, 1921. Triarylmethane dyes contg. hydroxyalkyl groups attached to N are obtained (1) by condensing Michler's ketone with an hydroxyalkyl-, hydroxyalkylalkyl-, or hydroxyalkylaralkylarylamine in the presence of P oxychloride; (2) by condensing Michler's hydrol with an hydroxyalkylarylamine of the types mentioned and oxidizing the resulting leuco compd. Suitable hydroxyalkylated amines are hydroxyethyl- or dihydroxyethyl-aniline, hydroxyethyl- α -toluidine, and hydroxyethyl- α -naphthylamine. Examples are given of the prepn. of basic blue to violet dyestuffs from Michler's ketone and hydroxyethyl- α -naphthylamine, and dihydroxyethyl-aniline, hydroxyethyl-aniline, hydroxyethylethyl-aniline, or dihydroxyethyl- α -toluidine.

Sulfonic acids of 2,3-hydroxynaphthoic arylides. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING. Brit. 183,428, May 23, 1922. Sulfonic acids of 2,3-hydroxynaphthoic arylides are obtained by sulfonating the parent arylides obtained as described in 13,237, 1913 (*C. A.* 8, 3864) and 23,732, 1913 (*C. A.* 8, 2780); they can be used in the manuf. of dyes. According to examples, β -hydroxynaphthylidide is sulfonated with H_2SO_4 of 66° Bé., and β -hydroxynaphthoic 4-chloro-2-toluidide with H_2SO_4 monohydrate.

Dyeing cellulose acetate. SOC. CHIMIQUE DES USINES DU RHÔNE. Brit. 183,806, May 17, 1922. Cellulose acetate threads, films, or fabrics, or mixed goods contg. them are treated, prior to, or during, dyeing, by means of Na_2PO_4 soln. The treated product may be mordanted with tannin and tartar emetic before dyeing.

Dyeing and printing. SOC. ANON. J. R. GEIGY. Brit. 183,813, July 7, 1922. Textiles or other materials are printed or dyed in fast colors by impressing cold or applying on a padding-machine readily sol. dyestuffs together with a concd. aq. soln. of a chlorinated HOAc or of glycolic acid or a mixt. of these acids, and fixing the color, without steaming, by allowing the material to dry and subsequently rinsing and drying it. Examples are given.

Printing textiles. CALICO PRINTERS' ASSOCIATION, LTD. Brit. 185,007, Aug. 13, 1921. Cotton fabrics are printed by mordanting with chrome and tannin, or equivs., dyeing with an appropriate dyestuff, and printing with discharge colors or pastes comprising caustic alkali with or without sulfoxylates, glycerol, and Rothelle salts for white discharge effects and together with vat colors for colored discharges, the fabric being then aged, washed, soaped, etc. In examples, the chrome-mordanted fabric is dyed or padded with tannin before, after or together with the dyestuffs, in which case Rothelle salts are included in the discharges; or the fabric is mordanted with tannin first

and then with a chrome mordant, or the two mordants are applied together. Suitable dyestuffs are chromazurines and chromophenines if the dyestuffs and tannin are applied together, these and in addn. alizarins if the tanning is subsequent to the dyeing, and prune and modern violet if the fabric is tanned before dyeing. The Provisional Specification refers also to the printing of silk fabrics.

Artificial threads; films; viscose. A. KÄMPF. Brit. 184,450, July 21, 1922. A spinning bath for use in the manuf. of artificial threads, films, etc., from viscose, consists of an aq. soln. of the acids obtained by sulfonating the resinous condensation products prep'd. by causing phenols to react with wood in the presence of acid catalysts. To the bath, mineral acids may also be added, or the acid may be partly neutralized, or to the bath may be added the salts of mineral acids or of the sulfonated acids above referred to; with these baths, satisfactory results are obtained with entirely unripened viscose. In an example, the bath contains 10-12% H_2SO_4 , 5% sulfonated acid, and 15% Na_2SO_4 ; and a spinning speed of 50 m. and a length of bath of 50 cm. are employed.

Artificial threads; films; viscose. A. KÄMPF. Brit. 184,449, July 21, 1922. A spinning bath for use in the manuf. of artificial threads, films, etc., from viscose, consists of an aq. soln. of the acids obtained by sulfonating the condensation products prep'd. by reacting with phenols on aldehydes and ketones, especially ketoses, aldoses, and more especially the various carbohydrates. The bath may also contain mineral acids or the salts of mineral acids and the sol. salts of the sulfonated acids. With these baths, satisfactory results are obtained even with entirely unripened viscose. In an example, a bath for use in making threads of about 2 deniers contains H_2SO_4 10, Neradol 8, and Na_2SO_4 10%; the bath is maintained at 18°, and a spinning length of 40 cm. with a normal speed of drawing is employed.

Viscose; artificial threads. TECHNOCHEMIE AKT.-GES. Brit. 185,493, March 4, 1921. Cellulose for use in the manuf. of viscose is subjected to a preliminary treatment with acid under the conditions specified and which are selected so as to avoid the production of hydrocellulose. The cellulose is heated for several hr. either with 0.5% HCl at 100°, or with 2% HCl at 80°, or with 8% H_2SO_4 at 40-50°, or with 0.2% H_2SO_4 at an excess pressure of half an atm., or in the case of bleached cellulose after immersion in 0.5% H_2SO_4 with subsequent heating to the b. p. The initial material is bleached or unbleached sulfite- or soda-cellulose. With cellulose treated in this manner, considerably smaller proportions of caustic alkali and CS_2 are required in the manuf. of viscose; the viscose soln. can be spun without ripening to give lustrous and strong threads; and in the case of unbleached cellulose, the brown dyestuff remaining in the threads acts as a mordant when the threads are dyed. Cf. 4713, 1896.

Artificial silk; viscose. GLANZFÄDEN-AKT.-GES. Brit. 185,718, May 20, 1922. To render innocuous the H_2S formed during the spinning of filaments from viscose solns., oxidizing agents, e. g., peracids or persalts, are added to the spinning bath. The process is particularly applicable to the spinning of unripened viscoses prep'd. from unripened alkali-cellulose, and especially to the production of very fine threads from such solns. by a drawing-out process.

Bleaching. H. B. SMITH. Brit. 183,424, April 1, 1922. Material such as cotton, cong. notes, shives, or leaf is bleached by bleaching as with an acid dye such as alk. blue and treating with an alk. oxidizing bath. Cf. 103,445.

Coated fabrics. L. MINYON. Brit. 184,845, May 9, 1921. Addition to 155,469 (C. A. 15, 1832). Fabric is coated with adhesive material (other than rubber) which is then dusted over with mica. The coating is then hardened by drying. Before being dried, the fabric may be printed, embossed or schreinered to imitate textile fabrics. According to the Provisional Specification, the mica may be incorporated with the adhesive before the latter is applied to the fabric, or it may be applied by printing on the coated fabric mica suspended in rubber, resin, or oil. Cf. 12,230, 1890.

Protecting animal fibers from alkaline liquids. AKT.-GES. FÜR ANILIN FABRIKATION. Brit. 183,868, Jan. 27, 1921. Animal fibers are protected from the action of alkalis in processes such as washing wool, degumming silk, mercerizing cotton in half-wool or half-silk fabrics, fulling wool, dyeing and printing animal or mixed fibers with vat or sulfurized dyestuffs, and finishing, dyeing, or improving skins or leather, by adding 1 or more of the following substances, in the proportion of not less than 3% by wt., of the goods treated: sugars such as glucose, fructose, etc., and sulfite cellulose, waste liquor, or the active constituents thereof.

Treating fibers. TECHNOCHÉMIA AKT.-GES. Brit. 183,249, April 20, 1921. Animal fiber, such as pig hairs, etc., is treated with Cl in known manner. The oxidized fiber, probably a polyhydroxyamino acid, is then dipped in a bath contg. excess of alkali such as NaOH, or Na_2CO_3 . The slippery transparent product is rinsed and, preferably after drying, treated with boiling soap soln., which produces a fiber of high luster, increased strength and elasticity, and having a soft and silky feel which may be enhanced by treatment with a little HOAc, or by calendering after drying. To the alkali bath may be added soaps, molasses, glucose, glycerol, or other substances which have a softening action. The treated fiber may be subsequently impregnated with a waterproofing and softening agent.

Treating animal fibers. TECHNOCHÉMIA AKT.-GES. Brit. 183,270, April 27, 1921. Addition to 183,249 (preceding pat.). The animal fiber is first treated with a large excess of oxidizing agent, rinsed, and then treated with a boiling soln. of soap or of a solubilized oil such as a sulfonated oil. In oxidizing, 150 kg. of CaOCl_2 may be used for 100 kg. of fiber.

Mixed-fiber textiles. TECHNOCHÉMIA AKT.-GES. Brit. 185,238, June 4, 1921. Animal fibers treated with an oxidizing agent and an alkali, as described in 183,249 (cf. 2nd pat. above) and 183,270 (cf. above), and mixed with artificial cellulose fibers, yield a textile material having the appearance of being made of one kind of fiber.

Treating fibers with liquids. J. BRANDWOOD, T. BRANDWOOD and J. BRANDWOOD. Brit. 182,575, April 8, 1921. Loose textile material in the unspun state is dyed, bleached, or otherwise treated by passing it below the level of the liquor in the treating tanks in lap or equiv. packed form between flexible open woven or meshed conveyors forming a container held in tight contact with cylindrical or plane perforated surfaces, or both which are arranged in the tanks, means being provided for closing any perforations not covered by the container. Treating liquid or air is passed through the perforated surfaces, the container, and material held therein. A suitable construction is specified.

Degumming silk. SOC. ANON. POUR L'INDUSTRIE CHIMIQUE À BALA. Brit. 184,788, July 24, 1922. Silk fabrics contg. raw silk interwoven with silk dyed with vat dye-stuffs are prevented from bleeding during degumming by the addn. of a persulfate to the bath. In the example given, silk dyed with china violet B is boiled with 10 times the quantity of raw silk for 2 hr. in a bath contg. per l. 15 g. of Marseilles soap and 2 g. of $\text{K}_2\text{S}_2\text{O}_8$.

Treating animal fibers for spinning etc. A. O. TROSTEL. Brit. 183,885, Feb. 26, 1921. To obtain a product suitable for spinning, felting and shrinking under the action of heat, animal fibers are immersed in the cold for about 2 weeks in a weak alk. bath. The bath may contain less than 0.5% alkali composed of milk of lime in admixt. with alkali sulfide. The fibers, preferably washed to remove the alkali and deposited impurities and then further treated in a dil. acid bath for about 24 hr., are finally washed and dried at a temp. less than 120° F. The product may be further treated for fire-proofing or other purposes with mineralizing agents such as chrome salts, a suitable bath comprizing a salt soln. contg. 1-6% of Cr_2O_3 by wt. and having a basicity equiv. to 1 hydroxyl radical. Cf. 4,144, 1879.

26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

Mineral coloring matters in Egypt. *Mining J.* 138, 825(1922). A plant at Helouan, near Cairo, is making dry colors and mixed paints. O. P. R. O.

Mineral colors in India. J. C. BROWN. *Bull. Indian Ind.* No. 22 (1922). O. P. R. OGLVIE

The production of naphthalene-formaldehyde condensation products and some of their technically important properties for the varnish industry. P. POLCHI. *Chem.-Ztg.* 46, 714-5(1922).—A brief review. F. A. WERTZ

The evaporation of volatile solvents. HANS WOLFF AND CH. DORN. *Farben-Ztg.* 28, 31-3(1922).—The rate of evapn. at room temp. of various volatile solvents, and of these solvents from oil and resin solns., was detd. gravimetrically, and by noting the time required for evapn. of a definite no. of drops of the solvents on filter paper. Results are plotted. The drop method gives correct relative speeds of evapn. for homogeneous solvents; the b. ps. of solvents give no indication of relative rates of evapn. at room temp.; benzenes evap. more rapidly than aromatic hydrocarbons of the same b. p.; the final portions of solvent evap. more slowly from oil and resin solns., and the same solvent evaps. at different rates from solns. of different resins. Cf. C. A. 16, 2610. F. A. WERTZ

Polymerization of fatty oils. J. MARCUSSON. *Z. angew. Chem.* 35, 543-4(1922); cf. C. A. 15, 318.—Oils kept free from air in daylight underwent an intramolecular polymerization; the I no. dropped and the sp. gr. increased. Ultra-violet light causes a more rapid polymerization, Chinese wood oil in the absence of O forms a white mass m. 32°, which cannot be considered a polymerized product as the I no. and sapon. no. are unchanged. The fatty acids from this product, m. 71° and consist of β -eleostearic acid which is the isomer of α -eleostearic acid present in the original oil. The formation of β -eleostearic acid is similar to the transformation of allocinnamic acid into cinnamic acid in sterile storage. By extg. the polymerization product with acetone and saponifying the residue and acidifying, thick oily to soft waxy fatty acids are obtained of I no. $\frac{1}{4}$ that of eleostearic acid and double the mol. wt. The sp. gr. is greater than 1. The property of wood oil first to form isomers under the influence of light and then to polymerize can also be observed in the drying process. By putting a thin coating on glass there appear after several hrs. ice-like crystals which eventually permeate the entire mass. They consist of β -eleostearin, which hinders drying. For use in the lacquer industry wood oil is heated to a high temp. to prevent the formation of β -eleostearin. The polymerization following the drying of fatty oils is intramolecular; the film contains unchanged oil, free fatty and hydroxy acids and neutral polymerization and oxidation products. H. SCHERUBEL

The development of industrial electric heating for low temperature enameling. W. S. SCOTT. *Trans. Am. Electrochem. Soc.* 42, preprint (1922).—Early expts. are recorded which point out the great importance of adequate ventilation of an elec. enameling oven. During the drying of the enamel combustible gases are evolved and these must be withdrawn in such a way as to avoid explosions. The suspensions and arrangement of the heating units are discussed. Typical elec. oven installations of the automotive and typewriter industries are illus. and described in detail. Cf. C. A. 16, 3263. C. C. F.

Ferric oxide (Brit. pat. 183,323) 18. Phenol-aldehyde condensation products [as varnishes] (Brit. pat. 184,961) 18.

Paints. F. GUNTER. Brit. 183,177, March 7, 1921. Paints which may be dild. with H_2O for use comprize a pigment, a medium such as a drying oil or a soln. of resin, H_2O , and a stabilizing agent sol. in H_2O and in the medium. The stabilizing agent may be a volatile substance such as alc., pyridine, acetone, or naphthenic acid, with or without an admixt. of a less volatile agent, such as glycerol or Turkey red oil, or it may be an NH_4 or alkali soap of a resinous acid or of a drying fatty acid. When alkali soaps are used as stabilizing agents, an oxidizable non-metallic element such as S, P, or Se is added, thereby producing acids which act on the soaps and produce insol. compds. The fatty acids set free from the soap by this reaction may themselves function as the binding medium. Oils partly hydrolyzed by means of enzymes such as are found in castor oil seeds may be used as media, the free glycerol present acting as stabilizing agent. The ingredients may be initially mixed without H_2O , and the stabilizing agent may be omitted and dissolved instead in the H_2O for diln. Suitable binding agents are linseed oil, hemp-seed oil, poppy oil, walnut oil, and wood oil.

Aluminium paint. H. O. ARMISTON. Brit. 184,909, Aug. 9, 1921. A paint consists of 4 oz. of powd. Al mixed with 8 oz. of shellac dissolved in 20 oz. of methylated spirit. Cf. 25,675, 1896, and 9273, 1910.

Titanium complexes and method for producing same. H. H. BUCKMAN. Can. 225,569, Nov. 7, 1922. In the production of composite pigments contg. Ti complexes, the pptn. of the Ti compds. on particles of $BaSO_4$ is effected at a temp. above 100° and under a pressure above atm.

Separating thallium and radioactive metals from lead ores and making a white lead pigment. J. B. HANNAY. Can. 225,160, Oct. 24, 1922. Pb ores contg. Ti and radioactive metals are volatilized with hot CO and N or other non-oxidizing gases and the fume produced is mixed with a large excess of air just after leaving the heating zone. The oxidized fumes are gradually cooled and the deposits formed are successively collected in a series of settling chambers. A pigment of the approx. compn. $3PbSO_4 \cdot PbO$ is obtained. The deposits carrying Ti and radioactive materials are again subjected to the same operation to effect concn.

Inks; paints. A. DE WAELE. Brit. 183,513, March 19, 1921. Inks and other pigmenting and like compns. for printing, duplicating, etc., comprize as the vehicle for the coloring matter an emulsion or emulsoid in the form of a plastic solid, of which the yield value (defined as the finite pressure it is necessary to apply before any flow through a capillary orifice takes place), is materially greater for the emulsion than for its components, the yield value of the components being, e. g., zero. The compn. may have the property of breaking down when brought into contact with paper or other porous material, one of the components being absorbed thereby. One of the components may be an oleaginous material, such as Yorkshire grease, wool fat, wool wax, a wax such as Japan wax or beeswax, or a soap insol. in H_2O , and the other component may be H_2O , the components being emulsified with or without the use of emulsifying agents.

Printing-surfaces. H. HUKWITZ & Co. Brit. 184,812, Aug. 19, 1922. A printing-surface for copying documents is produced by prepg. on a rigid surface a coating of a metallic salt and applying thereto an original which has been produced with an alk. or other ink which will combine with the salt soln. to form insol. oxides, hydroxides, or other compds. which will retain fatty ink or color. In one example very dil. HCl is rubbed on to the surface of an Al plate and an original, written in an ammoniacal ink, is then laid upon the plate. After removal of the original, the plate is rolled or rubbed with fatty ink. In another example, a silvered plate of brass or Cu is treated with dil. HNO_3 , and in a third example an Fe plate is treated with a mixt. of HCl, H_2SO_4 and HNO_3 .

Varnish for tracing cloth. GRUNER & REINHARDT Ges. Brit. 184,173, July 26, 1922. Tracing cloth is rendered resistant to H_2O by coating with a varnish consisting of collodion, a thinner, amyl acetate, and gum. In an example, ether is an ingredient.

Synthetic resins. D. G. ANDERSON and R. MACLAURIN. Brit. 183,629, May 17, 1921. Resinous products are obtained by condensation of $HCHO$ with the monobydric phenols boiling at $230-320^\circ$ obtained from the tar oils produced by low-temp. distn. of coal; the usual condensing agents, such as NH_3 , $NaOH$, or acids, are employed. The products are sol. in cold benzene. Cf. 24,426.

Synthetic resins. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE GES. Brit. 184,442, July 5, 1922. Addition to 182,450 (C. A. 16, 4358). Synthetic resins obtained by the condensation or polymerization of aldehydes with alkali are rendered stable toward H_2O by treating them in a state of fine subdivision with H_2O , to which a little acid is preferably added. The products are sol. in fatty oil, spirit, benzene and other solvents used in the manuf. of varnishes; by rolling in the soft state they can be converted into the com. form of sheet shellac. According to the example, the resin resulting from the condensation or polymerization of AcH is ground in a ball mill with a 3% aq. soln. of $HOAc$, the product filtered off and either melted or dissolved in a spirit or oil solvent.

Synthetic resins. SHAWINIGAN LABORATORIES, LTD. Brit. 183,830, July 25, 1922. Synthetic resins are formed by the direct action of C_2H_2 on phenol or its homologs in the presence of acid and a Hg salt. C_2H_2 , preferably in excess, is passed into a mixt. of the phenol with a little acid, such as H_2SO_4 , or an acid salt to which mercurous or mercuric oxide or sulfate has been added; the temp. is preferably maintained at $50-120^\circ$; increased pressure may be employed; a solvent for the phenol, e. g., glacial $HOAc$, an alc., or acetone, may be present. Examples are given in which phenol and cresol are the starting materials, the resulting product being finally rendered infusible and insol. by any known method.

Artificial resins. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE, GES. Brit. 185,107, Aug. 15, 1922. By subjecting resins obtained from aliphatic aldehydes to oxidizing treatment, products are obtained which, like shellac, are sol. in aq. solns. of borax and soda. The aldehyde resin may be oxidized in the molten state, or dissolved or suspended in a liquid, and a catalyst may be present. The products may subsequently be hardened by heating or other means, and are useful for the manuf. of oil varnishes. According to examples, (1) aldehyde resin is dissolved in glacial $HOAc$ and either ozonized O is passed in, or a little Mn acetate is added and O led through, the products in each case being pptd. by the addn. of H_2O ; (2) O is passed into a suspension of aldehyde resin in H_2O contg. a little $KMnO_4$ and the product is sepd.

Phenol-formaldehyde resins. A. HEINEMANN. Brit. 184,964, July 27, 1921. To render phenol-formaldehyde resins more stable chemically and physically, the resin, free from H_2O , is melted and dry powd. alkali glycerate stirred in until the whole is homogeneous. If more than 2% of glycerate is added, an insol. fusible resin results.

27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL

Technical aspects of hydrogenation. E. R. BOLTON. *J. Soc. Chem. Ind.* 41, 384-7R (1922).—Economy and efficiency of hydrogenation depend on a careful attention to the purity of the oil. A low temp. of reduction (250°) increases activity but renders the catalyst more susceptible to poisons; a high temp. of reduction (350°) lowers the activity of the catalyst but increases its life. The presence of H_2O in the oil causes hydrolysis and the fatty acid produced will form a coating of metallic soap which hinders

hydrogenation. For the reactivation and recovery of the catalyst processes have been suggested whereby both the oil and the Ni are recovered from residues in a condition suitable for immediate re-use. A large amt. of engineering skill has been directed to the designing of apparatus for violent agitation during hydrogenation but it seems obvious that once the catalyst has become impregnated with oil, H can reach it only by penetrating the oil and to do this it must be in soln. in the oil. This explains why such excellent results are obtainable with a gentle circulation of H-satd. oil. The main types of plants devised are: (1) a vessel nearly full of oil contg. catalysts through which H is circulated mechanically, (2) a vessel full of H into which an intimate mixt. of oil and catalyst is sprayed, (3) vessels contg. stationary catalyst through which oil and H are circulated. It has been suggested that poisoning of a catalyst by S from impure oils is proportional to the mass of catalyst while hydrogenation is a function of surface only. This being so it would be expected that a catalyst with relatively a large mass in proportion to its surface would harden oil contg. small amts. of poisons almost independently of these poisons. B. gives some curves showing the results of hardening oils by means of Ni wool which lend support to this view.

E. SCHERUBEL

Hydrogenation of fats. E. F. ARMSTRONG. *Chem. Age (London)* 7, 528(1922).—A review on fat hardening, the manuf. of H and the treatment of the catalyst.

E. SCHERUBEL

The manufacture of anhydrous and hydrous wool fat. K. F. EHMANN. *J. Am. Pharm. Assoc.* 11, 188-9(1922).—Description of pharmaceutical and chemical methods.

L. F. WARREN

The determination of the melting point of neutral fats. VICTOR BOULEZ. *Mat. grasses* 14, 6250(1922).—A glass tube is drawn out and passed through a round piece of cork of such a size that the two sink when immersed in water if the lower opening is open and float if it is closed. Draw a little of the molten fat up the point, allow to solidify, immerse in water which is slowly heated, and observe the temp. at which the tube sinks. The method is not suitable for testing very viscous substances, e. g., paraffins wool grease, etc., which adhere strongly to the glass. Cf. Racine, C. A. 16, 3005.

A. P.-C.

Commercial copra. (Miss) BONERY. *L'agronomie commerciale*, March 1922; *Industrie chimique* 9, 454(1922).—Samples from Seychells, Singapore, Togo, Mozambique, Ceylon, Zanzibar, Manila, etc., were analyzed. Moisture varied from 3.07 to 4.80%, fat from 62.82 to 71.06%. The av. for 10 samples was: H₂O 3.92%, ash 1.67, fat 66.41, protein 6.30, saccharifiable matter 11.00, crude fiber 1.878, undetd. 8.82.

A. P.-C.

Use of sulfur fumes in copra drying. A. H. WELLS AND G. A. PERKINS. *Philippine J. Sci.* 21, 49-53(1922).—A description is given of certain modifications of the sulfur-fuming box, the S burner, and prepn. and drying of the nuts. The H₂O content of sulfured copra is 5% and the % of free fatty acids is less than 1. The SO₂ partly evaps. during drying and partly oxidizes to H₂SO₄, which remains in the press cake. About 1 kg. of S per 3000 nuts is used and no trouble is encountered in expressing the oil or in using the cake for animal feed. The direct protection afforded by SO₂ does not last more than 1 mo. The prevention of mold by sulfur-fuming also prevents spoilage by beetles and it should be done soon after the nuts are opened if rainy weather is anticipated. E. S.

Refining of salt crude glycerol. W. E. SANGER. *Chem. Met. Eng.* 27, 827-32 (1922).—A description of the operation of the open and closed distn. systems for dynamite glycerol is given as well as the manuf. of chem. pure and yellow distd. grades. The bleaching of glycerol is discussed; and an outline of a complete method of treatment for still foots is given as follows: The foots are treated with a small amt. of Na₂CO₃ and filtered, the soln. is run into Pb-lined tanks and 60° H₂SO₄ is added. The amt. of

acid to be added is detd. in the lab. by treating 8 samples with varying amts. of acid, allowing to stand several hrs. and observing which one shows the best sepn. of tarry matter on top. The tank is then treated accordingly and the tarry matter skimmed off, and the strongly acid foots are transferred to a wooden vat where they are treated with $\text{Ca}(\text{OH})_2$. The mixt. is filtered to remove $\text{Ca}(\text{OH})_2$ and Ca soaps, the filtrate being run to a tank, where Na_2CO_3 is added to remove excess $\text{Ca}(\text{OH})_2$. This ppt. is filtered off and the filtrate transferred to the spent soap lyes to be again concd.

E. SCHERUBEL

Stability of sulfonated oils toward acid and lime. W. HERBIG. *Z. deut. Oel-Fett-Ind.* **42**, 646-8(1922).—W. proposes 2 new methods, based on very extensive lab. expts. simulating factory conditions. (1) *Acid stability*.—Weigh 2 g. of the oil into a beaker of 6 cm. diam. and 12 cm. height; add 198 cc. H_2O and place under it a ruled paper with lines 0.25 mm. wide. Titrate the soln. with $N \text{H}_2\text{SO}_4$ against methyl orange to redness, then dropwise until the first opalescence appears, noting the buret reading; then further to strong opalescence, again noting the reading, and finally to distinct turbidity, when the lines on the ruled paper disappear, again noting buret reading. Repeat the test at 30°, 50°, 70°, 90° and reheat during titration at 70°, and 90°, to prevent any drop in temp. Express the results as SO_2 required per 10 g. oil, plotting them as graphs. (2) *Lime stability*.—Bring the samples to a uniform fat content (best to 30%) and prep. 3 aq. solns. of 100 cc. each contg. 1, 5 and 10% of sulfonated oils, and exactly neutralize with caustic and phenolphthalein. Then prep. a hard H_2O of 120 German degrees by neutralizing lime H_2O with H_2SO_4 and titrate the oil solns. with this hard H_2O for turbidity as directed in (1), and make 3 tests at 20°, 50° and 90°. Express the results as CaO required per 10 g. of oil and plot on coordinate paper. P. ESCHER

True waxes. ERWIN KOCH. *Z. deut. Oel-Fett-Ind.* **42**, 630-1(1922).—True waxes are compds. of high mol. fatty acids with monovalent high mol. alcs. of the aliphatic or the aromatic series. Japan wax, however, contg. glycerol, is a fat, and wool fat, contg. no glycerol, is a wax. For the identification of waxes the acid no., sapon. no., and ether no. are detd. besides their phys. consts. In the case of beeswax the ratio of acid no. to ether no. is also detd.

P. ESCHER

Hexalin and methylhexalin in the manufacture of fatty preparations for the textile industry. WELWART. *Seifensieder Ztg.* **49**, 611-3(1922).—A discussion of the value of hexalin soaps and hexalin textile fats. Textile soaps contg. 10% of hexalin or methylhexalin remove mineral oil, dirt, etc., from wool much more readily and thoroughly than any other known prepn. The use of soda in washing becomes superfluous, and hard waters form no Ca-Mg soaps. When hexalin or methylhexalin is mixed with mineral oil and a small amt. of soap, they form clear solns. which can take the place of the customary fat prepn. used in the textile industry, and may be washed out of the fiber with lukewarm H_2O , without any soap at all or with small quantities. P. E.

Washing compounds in hard times. H. KÜHL. *Seifensieder Ztg.* **49**, 677-8(1922).—A discussion of soaps heavily filled with organic and inorganic colloids, with recipes for their manuf. P. ESCHER

Some technically important properties of hexalin soaps and their application. WELWART. *Seifensieder Ztg.* **49**, 649(1922).—Liquid hexalin soaps dissolve mineral oils and then form a clear soln. with H_2O . When much mineral oil has been used, they yield permanent emulsions with H_2O . They also dissolve or emulsify fats, sulfonated oils, resins, waxes, asphalt, tar and all kinds of dirt particles. These properties make hexalin soaps valuable for the textile industry, surpassing Turkish red oil in many effects, and are valuable in wool- and cotton-drying, bleaching and mercerizing. P. E.

Use of naphthenic acids in soap making. EUGENE SCHUCK. *Mat. grasses* **14**, 6249-50(1922).—Brief description of the prepn. of naphthenic acids from petroleum and of their uses. A. P.-C.

Soap diseases and their cure. O. SPANGENBERG. *Z. deut. Oel-Fett-Ind.* **42**, 645-6, 662-4(1922).—A popular account of the more common faults of soaps and their prevention, including soft feel, bad odor, dark color, poor lathering, high alkali, and poor soly. of laundry soaps and cracking and scaling of toilet soaps. P. E.

Adsorption and catalysis in fuller's earth (RIDEAL, THOMAS) **2**. Vegetable oils as motor fuels (MATHOT) **21**. By-products of industrial abattoirs; modern butchering installations and the utilization of animal blood (A. B.) **12**. The constitution of soap solutions (NORRIS, FALKNER, PRICE) **10**. Preparation of motor fuel from vegetable oils (MAILHE) **21**.

Extracting fats. S. ZIPSER. *Brit.* **183,825**, July 21, 1922. In the extn. of fats by volatile solvents the ext. is forced out of the extractor by solvent vapors, preferably those from the still in which the ext. is distd., aided or not by a suction pump. The ext. may be preheated before admission to the still by waste vapors from the still and extractors, the residual solvent may be removed by steam or by solvent vapors, and preferably all operations are carried out without admitting air to the app. A suitable app. is specified.

Extracting fatty oils. W. J. MELLERSH-JACKSON. *Brit.* **184,621**, June 3, 1921. "Cakes" are formed by compacting charges of the cotton seed, copra, or other meal in a die between perforated and grooved metal plated with attached fabric. The cakes, with the plates attached, are then packed in the oil-extg. press.

Purifying oils. V. F. FEENEY. *Brit.* **185,247**, June 13, 1921. In purifying animal, vegetable, or mineral oils by ozone supplemented or not by warm air and sunlight, the oil is showered through and filmed down the sides of a preferably glass-panelled chamber against a current of ozone-laden air. The oil then passes by a pipe to a reservoir in which it is heated and agitated prior to being pumped through the pipe and sprayer-pan for retreatment, or through a pipe to be heated and agitated with diatomaceous earth or the like in a tank and filtered in a press. Warm air may be sent through the chamber before, during, or after the treatment with ozone. The used air, etc., escapes through pipes to a stack. Pressure may be created in the chamber by adjusting the damper.

Regenerating fuller's earth, charcoal, and catalysts. E. R. BOLTON and E. J. LUSH. *Brit.* **185,174**, May 24, 1921. Fuller's earth, charcoal, and like purifiers of fats and fatty oils, and nickel or other catalysts used in hydrogenating fats and fatty oils, are regenerated by treatment with superheated steam until their temp. is 230-300° so that the oil is hydrolyzed and glycerol and fatty acid distil over. To reduce the loss of glycerol the steaming may commence under pressure, which may later be reduced to or below atm. to promote distn. The oil-free fuller's earth or charcoal may be treated hot with air to char org. impurities, and then with steam, preferably superheated, before cooling. A suitable app. is specified.

Synthetic waxes. G. SCHICHT AKT.-GES. AND A. GRÜN. *Brit.* **183,186**, March 17, 1921. Mixts. of alcs., aliphatic acids, esters, and hydrocarbons, all of high mol. wt., which approx. in compn. to vegetable waxes are produced by oxidizing hydrocarbons such as paraffin, ceresin, bitumin, etc., with O or O-contg. gases at a temp. of at least 150°. A little acid such as stearic acid may be added to assist the reaction. The product is freed from liquid substances by pressing or by washing with slightly dild. alc. E. g., paraffin melting at 50° is heated for 6-8 hr. with excess of moist or dry air to 150-155°, or hydrocarbons of higher m. p. are heated for 4-5 hr. to 100°.

Soaps. B. J. A. NIJDAM. *Brit.* **183,837**, July 26, 1922. White inodorous soap is produced from soaps made from refined or unrefined oils, fats, and fatty acids, or waste

products of oil and fat manuf., or from soap stocks obtained in de-acidifying fats and oils, by spreading aq. solns. of these materials over surfaces such as plates or rollers heated *e. g.*, to 90–150°. By treating a thin film of soap at 100°, a dry product is obtained which on cooling takes the form of flakes. By using a lower temp. and a thicker layer of the soln., the amt. of residual moisture can be regulated, and soap in pasty condition, suitable for making cakes or bars, is obtained.

Cleansing-compositions. E. CHAMBERLIN. *Brit.* 184,248, May 3, 1921. A detergent and disinfecting soln. for removing grease or dirt from domestic or other utensils, and for deodorizing purposes, is made by boiling together in H₂O a mixt. of Na₂CO₃, KMnO₄, and animal charcoal. The resulting soln. is allowed to settle, and is decanted and filtered until a clear soln. is obtained.

28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

Sugar purity determinations. W. D. HORNE. *Louisiana Planter* 69, 265–6; *Facts About Sugar* 15, 333–9(1922).—A special Brix spindle is described which rectifies some of the common sources of error in purity detns. Accurate Brix readings corrected for temp. are possible to about a hundredth of a degree. Combined with the use of the dry lead subacetate, rapid and accurate results are obtainable. C. H. C.

Purification of beet sugar juices. C. G. LEONIS. *Sugar* 24, 440–1(1922).—With clean beets which are cut up into uniform sized cosettes, best extn. of sucrose is obtained below 83°. The ratio of non-sugars to sugar is least when rapid extn. at 80° is practiced. Juices of higher purity are obtained through osmotic action rather than through the extn. of disrupted cells. The application of heat to the extn. cell next to the head is best. C. H. C.

The double carbonatation process; its application to the cane sugar industry. H. M. PEZZANI. *J. fabr. sucre* 63, No. 37(1922).—The uba cane juice of the Natal plantations has an unusually low glucose content. For this reason it is suggested that instead of the present method of refining wherein the juices and sirups are kept acid in reaction, a method similar to the French method of making beet sugar might well be adopted. This calls for double carbonatation and sulfitation so conducted that the juices and sirups remain slightly alk. at all times. L. E. GILSON

Barium sulfate and the desaccharification of molasses. MANOURY. *J. fabr. sucre* 63, No. 35(1922).—The BaSO₄ is reduced by heating with powd. coal in the usual way and then treated with hot H₂O forming a soln. of Ba(SH)₂ + Ba(OH)₂. Treatment of the soln. with ZnO or Zn(OH)₂ yields a ppt. of ZnS and a soln. of Ba(OH)₂. The latter is used to ppt. a mono-barium sucrate in the usual way. The washed sucrate is treated with ZnSO₄ soln. (made by the action of dil. H₂SO₄ on the ZnS obtained above) and the sucrose soln. filtered off from the BaSO₄ + Zn(OH)₂ ppt. which forms. The ppt. is used to treat a new lot of Ba(SH)₂ + Ba(OH)₂ soln., forming Ba(OH)₂ soln. and lithopone. The latter may be sold as such or may be treated with H₂SO₄ to form more ZnSO₄ soln. The process has been tried only on a lab. scale. The advantage claimed is in the avoidance of carbonatation of the Ba sucrate and the difficult and expensive recovery of the Ba carbonate. L. E. GILSON

The comparative sweetness and preserving quality of cane and beet sugars. J. P. OGILVIE. *J. Soc. Chem. Ind.* 41, 343–5R(1922).—The various grades of white cane and beet sugars may be divided broadly into refined and direct consumption sugars. By a refined sugar is generally understood a product which is obtained by remelting raw cane or beet sugar, passing the resulting liquor through animal charcoal to decolorize and purify it and finally recrystg. The sucrose content of such sugars is generally

99.95%. It is conceded by all that there can be no difference in the sweetness or preserving quality of such sugars whether they be derived from the beet or the cane. Direct consumption sugars are those produced directly from the cane or the beet without the intermediary of the refinery or the use of animal charcoal. Grades of sugar containing traces of acid, especially fruit acids and flavoring substances, may be sweeter than others. Low grade direct consumption sugar of the beet sometimes contains a trace of alkali and would be judged less sweet. Cane and beet sugar are equally suitable for preserving.

RUTH BUCHANAN

Chemistry of the polysaccharides. HANS PRINGSHEIM. *Z. angew. Chem.* 35, 345-9(1922).—A general discussion of starches, methylated starches, amyloses, glycogen, inulin and cellulose, in which P. reviews the work of his lab. and comments on the work of other investigators.

C. J. WEST

A report on the *Zamia* starch situation. J. F. CLEVELAND. *J. Am. Pharm. Assoc.* 10, 837-40(1921).—*Zamia floridana* D. C. grows wild in Florida. Its rhizomes are collected and starch is prepd. from them by the usual methods. Analysis of the air-dried rhizomes showed H_2O 7.73, ash 5.01, acid-insol. ash 0.90, Et_2O ext. 0.63, protein ($N \times 6.25$) 6.17, crude fiber 0.23 and N -free ext. 71.23%. By the diastase method 37.75% of starch was found. The starch from *Zamia* has been marketed as "Florida arrowroot." This term is likely to become misleading since the true source of arrowroot starch is the root of *Maranta arundinacea*, which grows in the West Indies and which mfrs. are now proposing to import for starch making in Florida. It is reported that the H_2O used in making starch from *Zamia* produces slow poisoning when used by animals.

L. E. WARREN

Determination of technical recoverable starch in starch pulp. E. PAROW. *Z. Spiritusind.* 45, 149(1922); *J. Soc. Chem. Ind.* 41, 512A.—Detn. of 12 samples of starch pulp by Klopff's method gave variable results. The moisture in 6 samples of dry pulp varied from 13.43 to 15.29%, and of 6 samples of moist pulp from 43.1 to 53.4%. Polarimetric detns. gave the most accurate results compared with total starch in dried samples detd. by the Märcker-Delbrück method. It is necessary to decolorize dark colored samples with charcoal before polarimetric readings can be taken. None of the methods employed gave consistent results under all conditions.

C. N. FREY

Extracting sugar and other substances. SOC. ANON. DES ETABLISSEMENTS, A. OLIER. *Brit.* 184,433, July 21, 1922. A machine for making exts. by the diffusion process, especially applicable for extg. sugar from beet or cane, consists of a closed conduit through which the material to be treated is carried in counter-current to the extg. liquid by an endless conveyer provided with perforated plates or buckets.

Crystallizing saccharine solutions. T. C. JACOBS. *Brit.* 185,707, March 30, 1922. In connection with a set of vacuum pans for sugar is provided a tank into which virgin grain from any pan can be passed, and afterwards transferred to any other pan to start crystn. therein. The tank may be placed at the level of the pans when it is closed, and can be exhausted so that the grain passes to it by suction, or it may be opened and placed below the pans, in which case the grain passes to it by gravity and is withdrawn by suction. The tank is provided with stirrers for treating the grain while cooling.

29—LEATHER AND GLUE

ALLEN ROGERS

Report of the commission on leather analysis. P. CHAMHARD. *Ind. cuir* 1922, 229-35; *Cuir* 1922, 333-5; *J. Soc. Leather Trades' Chem.* 6, 358-62(1922).—Three samples of each of 3 tanned hides were analyzed in 3 different labs. for hide substance,

mineral matter, water solubles, and fat. Good concordance was obtained on the same sample for hide substance and mineral matter, but not for the other detns. The differences between the hides which had been similarly tanned in different lots were too great for accuracy.

F. L. SEYMOUR-JONES

Hectographing on leather. PASCAL, HUC. *Ind. cuir* 1922, 313-5.—The hectograph paste is made from finely powd. kaolin, glycerol, water, and an antiseptic, *e. g.*, anidol. The hectograph ink may be made by triturating the dyestuff with concd. alc. and adding a warm soln. of glycerol in water, with or without AcOH. Its compn. will depend on the previous treatment and tannage of the skin. The skin must be entirely smooth and highly polished.

F. L. SEYMOUR-JONES

A note on "spued" leathers. P. HAMPSHIRE. *Bull. Bur. Bio-tech.* No. 6, 192-4 (1922).—Spue on leather may be (a) fat spues, where the fats in the leather are decomposed by oxidation or lipases or where the crystn. of the hard fats used in currying occurs; (b) damp spues, where the fat-liquor deposits on the grain of imperfectly dried goods; (c) glucose spues, from adulteration with glucose; (d) salt spues, where inorg. salts from the weighting of the leather or shoe fabric lining are deposited on the leather grain; (e) Na_2SO_4 spues, deposited from chrome and semi-chrome leathers where the shoe touches the foot and is moistened with perspiration; subsequent drying out concentrates the salt at the point of contact and crystn. occurs in the leather fibers with damage to the leather.

F. L. SEYMOUR-JONES

Uses of borax. ANON. *Raw Materials Review* 1, 170(1922).—Many uses of borax in the leather industry are described.

O. P. R. OGILVIE

The brine and pickling bath. R. ANDREIS. *La Conceria* Nos. 809-10; *Reprint Biblioteca del Conciatore* 1922.—An extensive report and discussion of the work of Eitner and Stiasny and of others on different chem. methods of pickling hides for different grades of leather.

C. C. DAVIS

Minor worries in the dyeing of gloves; blue spots. ANTOINE RIGOT. *Cuir* 1922, 373-5.—Blue spots on leather were traced to (a) iron dust from the emery used in cleaning the buffing wheels, (b) iron in the dust in the drying rooms from nailed shoes passing over the cement floor, (c) iron in the sawdust from sharpening the saw while over the sawdust pile.

F. L. SEYMOUR-JONES

The weight (specific gravity) of leather soles. E. ANDREIS. *Reprint Biblioteca del Conciatore* 1921.—A review of the chem. methods employed to control the d. of sole leather during tanning.

C. C. DAVIS

Analysis of tanning materials. III. V. KUBELKA AND B. KÖHLER. *Collegium* 1922, 167; cf. *C. A.* 16, 4088.—An investigation of the effect of concn. of tannin on analytical results by the official shake method, the shake method with double detannization, and the filter method. Samples of oak bark, pine bark, old and new gambier, and oak wood exts. were made up in solns. of 0.5, 1.5, 2.5, 3.5, 4.5, and 5.5 g. tannin per l., the amt. of tannin being reckoned from the filter method using 10 g. hide powder and 4 g. tannin per l. These were analyzed by the above 3 methods. Both shake methods give a variation in the amt. of non-tannin found with the concn. of tannin taken, while the filter method gives almost const. results independent of tannin concn. Assuming the adsorption theory of tanning, the shake method, even with double detannization, results in an equil., while in the filter method, provided excess of hide powder be used, the adsorption of tannin is taken to completion. The differences between the methods did not depend on the degree to which the hide powder was chromed. For the leather chemist "tannin" must be that matter taken up by the hide, and tannin analysis must consist in a kind of adsorption analysis whereby the matter taken up is sepd. from that not taken up. Hence the filter method is to be preferred to the official shake method.

F. L. SEYMOUR-JONES

Individual analytical characterization of tanning materials and extracts; determination of mixtures and adulteration. M. JAMET. *Ind. cuir* 1922, 236-55; *Cuir* 1922, 366-73; *J. Soc. Leather Trades' Chem.* 6, 336-50(1922).—The first part reviews the qual. analysis of tanning materials. New tests are required for recently introduced materials such as gonakieh and tizerah pods, since the latter exhibits all the reactions of quehracbo. An extension of color reactions with metallic mordants on cotton cloth is suggested. The second part reviews the special tests for mixts. and adulteration with cheaper materials. There is as yet no special test for tizerah, but it generally has a higher tans/non-tans ratio than quehracbo. It is proposed that the HCl-HCHO ppt. be dissolved in Na₂SO₃ or some org. solvent and the soln. further examd. as a means of sepn.

F. L. SEYMOUR-JONES

One-bath tanning with chrome alum. P. CHAMBARD AND L. MEUNIER. *J. Soc. Leather Trades' Chem.* 6, 288-96(1922).—See C. A. 16, 4091.

E. J. C.

The conditions for one-bath chrome tannage. P. CHAMBARD. *Ind. cuir* 1922, 197-206; cf. C. A. 16, 4091.—The manuf. of 1-bath chrome liquors is described. Expts. were made on the taking up of Cr₂O₃ and SO₃ from chrome liquors by hide, but the results are vitiated by the fact that amts. taken up were detd. by analysis of the residual liquor and not of the chromed hide.

F. L. SEYMOUR-JONES

Home tanning. R. W. FRY, I. D. CLARKE AND F. P. VEITCH. U. S. Dept. Agr., *Circ.* 230, 1-22(1922).—Directions are given for small scale tanning in the prepn. of bark-tanned sole and harness, chrome-tanned and alum-tanned lace leathers.

W. H. ROSS

The cultivation of tannin-producing acacias in French North Africa. JALADE. *Cuir* 1922, 329-32; *J. Soc. Leather Trades' Chem.* 6, 350-7.—Analyses were made of the bark and pods of various species of acacia (wattle) growing in Morocco. The barks showed tannin per cent: *A. pycnantha*, 42.1-44.0; *A. decurrens*, 33.9-34.9 (another sample gave 38.7-42.7); *A. saligna*, 20.4; *A. cyanophylla*, 11.7; *A. lophanta*, 18.8. The pods showed: *A. decurrens*, 29.6; *A. floribunda*, 11.0; *A. saligna*, 14; *A. longifolia*, 11.6; *A. lophanta*, 5; *A. cyanophylla*, 2. Lab. tanning tests with *A. lophanta* and *A. decurrens* gave a good product of a pleasing color.

F. L. SEYMOUR-JONES

By-products of industrial abattoirs; modern butchering installations and the utilization of animal blood ("A. B.") 12. Solidifying fibrous pulp (Brit. pat. 185,399) 23.

Tanning. P. J. C. MARGOTTON. Brit. 184,955, June 30, 1921. Unhaird hides are tanned, especially for the production of glove-leather, by treating in a fulling app. with chromic acid, H₂SO₄, and H₂O, then draining, treating first with acid reducing gases or vapors and then with alk. gases or vapors, washing, subjecting to a chamoizing treatment, degreasing, wringing, and finally drying. The amt. of chromic acid and H₂SO₄ in the mixt. is proportional to the wt. of the hide, but the amt. of H₂O is const. A suitable app. is specified.

Chrome tanning. D. BURTON AND A. GLOVER. Brit. 184,360, July 26, 1921. Basic Cr salts for use in the chrome tanning or dyeing of leather are produced by the reduction of dichromates in HCl or H₂SO₄ soln. by means of tea-dust, before or after extn. of caffeine therefrom. The addn. of acid to the dichromate soln. generates heat, and the temp. of the soln. may be raised, if necessary, by the introduction of live steam. The addn. of tea-dust causes a vigorous reaction, which is complete when the color of the soln. changes from reddish brown to bluish green. In an example, 225 lb. of Na₂Cr₂O₇ dissolved in 40 gal. of H₂O are treated with 190 lb. of H₂SO₄ and 57 lb. of tea-dust, the reduction process occupying 5 hr. Acid or alkali may be added, if necessary, to bring the soln. to a standard basicity.

Synthetic tanning agents. R. B. CROAD, G. E. KNOWLES and H. M. McARTHUR & Co., LTD. Brit. 182,823, Jan. 3, 1921. At least two mols. of an aromatic hydroxy compd. are condensed with 1 mol. of HCHO with an alk. condensing agent; the product is sulfonated with one to two mols. of H_2SO_4 and then partially neutralized. Crude cresol is given as an example of the aromatic hydroxy compd. oxides, hydroxides, carbonates, or bicarbonates of alkali and alk. earth metals, NH_3 , or alk. salts such as sodium acetate are referred to as condensing agents; as neutralizing agents, oxides, hydroxides, or carbonates of alkali and alk. earth metals, or NH_4OH or NH_4CO_3 , may be employed. Instead of HCHO, its polymers or compds. giving rise to it may be used; also the condensation may take place at ordinary or increased pressure. Cf. 171,729.

Synthetic tanning agents. R. B. CROAD and H. M. McARTHUR & Co., LTD. Brit. 182,824, Jan. 3, 1921. Sol. tanning agents are produced by first condensing at least two mols. of an aromatic hydroxy compd. with 1 mol. of HCHO by means of an alk. condensing agent, next sulfonating the resinous product with 1 or 2 mols. of H_2SO_4 , then condensing the sulfonated resin with an aldehyde and an aromatic compd. contg. 1 or more sulfonic acid groups alone or in combination with hydroxyl, halogen, or both, and finally partially neutralizing the product. For the first condensation, HCHO may be replaced by its polymers or compds. giving rise to it; while oxides, hydroxides, carbonates or bicarbonates of alkali and alk. earth metals, NH_3 , or alk. salts such as AcONa may be employed as condensing agents. The sulfonated aromatic compd. used in the second condensation may comprize the sulfonated resin of the first condensation; and the aldehyde in the second condensation may be HCHO or its polymers, AcH or its polymers, trithioacetaldehyde, aldol or crotonaldehyde. For the partial neutralization, oxides, hydroxides and carbonates of alkali and alk. earth metals, Zn and Mg , and NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ may be used. Crude cresol is given as the example of the aromatic hydroxy compd. employed in the first condensation; and crude cresol-sulfonic acids and crude α - and β -naphthalene-sulfonic acids are examples of the sulfonated aromatic compd. of the second condensation.

30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

Comparative tests with rubber compounded with sulfur and litharge. H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 4, 520-2(1922).—A control sample prepd. by AcOH and 10 samples prepd. by Na_2SiF_6 (cf. C. A. 16, 2621) were compared as regards rate of cure in a 90:10 rubber-S mixt. and in the same mixt. plus 50 parts PbO . Five of the latter samples had been packed dry and were received so; the other 5 had been packed wet and were received in a moldy condition. In the absence of PbO , the samples in the former group differed from the control but not among themselves; in the presence of PbO , they differed neither from the control nor among themselves. The samples in the latter group differed from the control, both in the presence and in the absence of PbO ; and differed among themselves more considerably in the presence than in the absence of PbO . Substances necessary for the full accelerating effect of PbO are partly destroyed by the growth of mold on rubber. (Cf. C. A. 16, 3011.) G. S. W.

Rubber as applied to aircraft. J. W. W. DYER. *India Rubber J.* 64, 595-603 (1922).—A survey of the chief applications of rubber to both heavier-than-air and to lighter-than-air craft. The phys. and chem. problems encountered are described for the following important uses: (1) gas-holding layer and outer protective layer for envelopes of balloons, non-rigid and semi-rigid ships; (2) adhesive for binding the gold-beaters' skin to the cotton fabric in gas bags of rigid ships; (3) shock-absorber cord and (4) gasoline hose. C. C. DAVIS

The proofing of fabric with rubber latex. H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 4, 402-6 (1922).—Untreated rubber deposited on fabric from latex absorbs moisture quickly and is probably of no practical value as proofing. If, however, the rubber film is soaked in water, so as to remove sol. constituents, and is then re-dried, it is much more resistant to water. Vulcanization of the film, by the aid of an accelerator at 100°, or by the Peachey process, improves the water-resistant properties of the untreated film, but not sufficiently for practical application. Vulcanization at higher temps. renders the film sufficiently resistant, but tenders the fabric. G. S. W.

Studies in vulcanization. Some further effects of acceleration on the rubber stress-strain curve. P. SCHIDROWITZ AND P. L. BEAN. *J. Soc. Chem. Ind.* 41, 324-6T (1922); cf. C. A. 16, 1033.—Results are now reported on the effect of varying the amt. of S, keeping the accelerator-rubber ratio const. and using piperidine piperidyliditbiocarbamate as before. To the basic compd., pale crepe 100, ZnO 2.5, accelerator 0.5, colloidal clay 1.5, 6 mixes were made contg. 1 to 4 of S. Cures of 1, 2.5, 5, 10, 20, 30 and 40 min. at 141° were made on each. Curves give the coeff. of vulcanization, % elongation at 600 and 1040 g. per mm.² and the breaking strength. Combination of S in all cases was comparatively rapid in the early stages, the steepness of the curve increasing with the total S. Reversion of the extensibility occurred at a comparatively early period when the S did not exceed 2.5%, the elongation increasing with the time of cure after a preliminary decrease. Judged by the breaking strength, moderate curing took place with 2.5% S, but below this %, the results were poor. It was previously shown (*loc. cit.*) that excellent cures were obtained with a min. of 2% S. It is concluded, therefore, that this accelerator requires 2-2.75% S to attain full activity, allowing for variations in materials and conditions. C. C. DAVIS

Spongy rubber. F. FLEUMER. *Brit.* 184,468, Aug. 8, 1922. In the process for producing rubber sponge by vulcanizing a mixture subjected to gas under pressure, the rubber is subdivided into particles, threads, plates, etc., as thin as possible to facilitate the permeation of the mass by the gas. Finely divided rubber is placed in molds capable of being compressed in an autoclave, and gas under pressure allowed to permeate the mass. The mass is partially vulcanized, mech. pressure is applied to the molds by a ram to cause the rubber particles to cohere, and the vulcanization is completed. The mech. pressure is removed and then the gas pressure, whereupon the gas entrapped in the pores of the rubber expands and forms cells. By mixing powders, threads, etc., of different colors, variegated effects may be obtained.

Spongy rubber. K. H. FULTON. *Brit.* 185,477, May 25, 1921. Finely divided charcoal is mixed with rubber, vulcanizing agents, etc.; the mix is treated with an inert gas, such as N, under pressure, whereby the gas is occluded in the charcoal; the compn. is vulcanized and allowed to cool while still under pressure; the pressure is removed and the product reheated. Suitable proportions are 3-5% of charcoal and 5-15% of S, Sb₂S₃, etc., according to the hardness required. For hard rubber the material is only partly vulcanized before the pressure is released, and the vulcanization is completed at the second heating. To assist the permeation of the mass by the gas in articles of considerable thickness, fibrous filaments are added to the mixing. Soft articles are preferably made from a mixt. of Para rubber and balata. The material is applicable to heat insulation, upholstering, tire fillings, etc.

Rubberized fabrics. P. BRITTON and GRIFFITHS BROS. & Co. LTD. (London), *Brit.* 184,578, May 17, 1921. Latex is used instead of rubber soln. in coating materials. It may first be applied to a backing and the film then transferred to the material to be coated. The film of rubber forms as the latex dries or is deposited therefrom; it may be washed and finally vulcanized. Compound fabrics may be made by uniting several sheets of coated fabric.

Hollow rubber articles. ROBERT RUBBER CO. Brit. 185,089, March 21, 1922. Hollow articles, particularly tennis balls, are vulcanized in a mold under internal fluid pressure, which shapes the article, and after removal from the mold, expands it to a predet. size at a predetd. pressure. Definite quantities of a gas-producing substance or mixt., *e. g.*, 0.7 g. of NaNO_2 and 0.532 g. of NH_4Cl , although an excess of the latter is generally employed, are placed in a tennis ball "center" in a mold, and on heating evolve N, which expands the center in the mold, and after completion of the cure and removal of the mold, expands the center further, and maintains a pressure of approx. 22.4 lb. per sq. in. above atm. Other gas-producing substances specified are (1) any NH_4 salt, and any nitrite, (2) Na_2O_2 and H_2O , (3) BaO_2 and acid, (4) H_2O_2 , (5) any org. compd. or mixt., which on heating evolves N, (6) an alkali and an NH_4 salt.

Fireproofing rubber, etc. H. FROOD and H. P. ALGER. Brit. 183,922, April 30, 1921. Rubber and rubber-like substances and compns. contg. them are rendered less inflammable by an admixt. of casein and hydrated $\text{Al}(\text{OH})_3$, preferably with the addn. of a small proportion of antimony chloride. The casein may be incorporated either as powder or mixed with borax soln. to form a plastic mass. Examples of compns. suitable for floor coverings are given, which compriz rubber, fibers such as cork and shredded cotton, ZnO or Fe_2O_3 , and S, in addn. to the fireproofing ingredients specified above.

Cores for tires. A. MALLABY. Brit. 185,240, June 8, 1921. A core for tires is formed of about 15 parts of rubber, 5 parts of S, 1 part of resin oil, and 15 parts of sponge waste, in the form of clippings of vulcanized rubber sponge, or of a mixing adapted to produce sponge on vulcanization, which is molded and vulcanized as usual.

Vulcanizers and vulcanizing. B. LAMBERT. Brit. 183,500, April 27, 1921. A eutectic alloy composed of Sn 25, Pb 16, and Cd 9 parts, which melts at about 145° and remains at this temp. until completely solidified, is employed for imparting heat to a vulcanizer. By melting a definite quantity of alloy, the temp. is maintained for a definite time. If a higher initial temp. is desired, an alloy consisting of 57 parts of Sn, 21 parts of Pb, and 22 parts of Cd is used. This melts at 153° and cools as it solidifies to 145° . Several forms of app. are described.

Vulcanizing apparatus. W. FROSR. Brit. 184,265, May 6, 1921. A heating unit is constructed with a heat capacity such that when raised to a temp. not less than vulcanizing temp. it maintains the article to which it is applied at the desired temp. for the length of time necessary to complete the vulcanization. The unit preferably comprizes a container, surrounded by heat-insulating material except on the working face, contg. a substance which changes its state and gives out its latent heat at the vulcanizing temp. Suitable substances are the alloys described in 183,500 (preceding abstract). Mixtures of substances having different m. ps., or mixts. which give eutectic alloys at appropriate temps. may also be used. Substances such as wax which are poor conductors of heat in the solid state are particularly suitable. The app. may be made sufficiently heavy to produce the requisite pressure when laid upon the article to be treated. Cf. 7477, 1894.

Puncture-sealing composition. H. H. WARMUND. Brit. 185,114, Aug. 22, 1922. A puncture-sealing compn. consists of concd. sulfite cellulose liquor of about $30\text{--}40^\circ \text{Bé.}$, which has been freed from CaO and Fe , a binding agent such as gum, and an earthy constituent such as talc. *E. g.*, 40–50 parts by wt. of sulfite liquor, 6–10 parts of a binding agent (gum), and 50–60 parts of an earthy substance (talc) are worked up at ordinary temp., passed through rollers to remove air, and if necessary filtered, and pumped into the tire. Pine essence may replace the sulfite liquor wholly or in part.

